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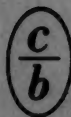
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Chemistry Section

ДОКЛАДЫ АКАДЕМИИ НАУК СССР

(DOKLADY AKADEMII NAUK SSSR)

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Chemistry Section

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IN ENGLISH TRANSLATION

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CATALYTIC POLYMERIZATION OF PROPYLENE-PROPANE
MIXTURES OVER PHOSPHORIC ACID ON KIESELGUHR

L. I. Antsus and Corresponding Member AN SSSR A. D. Petrov

In a number of earlier investigations, we have studied the polymerization of propylene and of mixtures of it with propane over zinc chloride [1]. Optimum conditions for the polymerization of propylene to trimer were determined, and it was shown that $ZnCl_2$ gives more branched nonenes than does H_3PO_4; as a result, the nonanes obtained by hydrogenation of the nonenes produced over $ZnCl_2$ had higher octane numbers. The structures of the nonenes were determined, and the polymerization mechanism was established. It was further found that the yield of the dodecene fraction formed over $ZnCl_2$ catalyst could be increased to 65% by decreasing the propylene feed rate; however, the degree of unsaturation of the polymerizate was simultaneously increased due to the formation of diolefinic hydrocarbons. When the space rate was decreased still further by dilution of the propylene with propane, a new reaction took place over $ZnCl_2$—dehydrocyclization occurred with the formation of benzene and isopropylbenzene in up to 30% yield [2] (probably as a result of contamination of the feed gas with sulfur compounds fromed from ZnS). It is interesting to note that aromatic hydrocarbons could not be prepared over H_3PO_4 under analogous conditions; moreover, it was found that in this case a decrease in space rate led to the opposite reaction—to the formation of saturated hydrocarbons accompanied by the deposition of carbon on the catalyst (see the data of Table 1). Thus, it became quite clear that $AnCl_2$ and H_3PO_4 are basically different catalysts with respect to olefins.

Our search was for conditions for polymerization of propylene-propane mixtures without formation of saturated hydrocarbons and without deposition of carbon using a commercial catalyst—phosphoric acid on kieselguhr. From the experimental data presented below it may be seen that space rate has a most important effect on the nature of the polymerization, the yield of polymerizate, and the fractional composition of the polymerizate. The optimum space rate depends on the ratio of propylene to propane in the feed gas and on the polymerization temperature. With 83% propylene and a space rate of 2-2.5 liters per liter of catalyst per hour, the polymerizate yield was 2-1.5 liters per hour. At a lower space rate, 1 liter per liter of catalyst per hour, the polymerizate yield dropped to 0.7 liter per hour. It is interesting to note that in the case of $ZnCl_2$ under these same conditions, the yield of polymerizate was only 0.3 liter per hour. With 50% propylene and a space rate of 2.0-3.2, the total yield of polymerizate varied in the range of 0.86 to 1.2 liters; i. e., it was somewhat lower, as would be expected. However, the yield of the desired fractions (tetramer and pentamer) was increased under these conditions by a factor of 1.5-2 and reached 44-48% per pass (without recycle). The optimum temperature for polymerization to olefinic products was 175-200° under the experimental conditions indicated above. It is interesting to note that not only at temperatures above 220° (even at high space rates, 2.0-3.0), but also at low temperatures (150°) and low space rates (0.6-0.7), hydrogen transfer occurred with the formation of unsaturated hydrocarbons and coke, in the first case, and of polymers, in the second case. Moreover, in the second case there was rapid swelling of the catalyst apparently owing to excess moisture (the removal of which was difficult at 150°). It is not difficult to see that the selection of the optimum space rates and temperatures for the different mixtures of feed gases is decisive as regards the normal course of the process and the attainment of optimum yields of tetramers and pentamers. Finally, it should be pointed out that H_3PO_4 is significantly less subject to poisoning by sulfur impurities in the feed gas than is $ZnCl_2$.

Besides the yield of the desired fractions, branching of the hydrocarbons is of considerable interest; minimum branching of the polymers is desirable when detergents are being synthesized, while, on the other hand, maximum branching is desired when the products are to be used as surface-active agents. For evaluation of the

TABLE 1

Expt. No.	Space rate in liters per liter cat. per hr.	Yield in ml per kg cat. per hr.	Tetramers and pentamers (fracs. with b.r. > 150°), % of polymerizate	Change in nature of polymerizate during prolonged catalyst use
				83% propylene
1	1.0	766		Content of unsaturates did not
2	1.71	1141	} 25–30	increase; quantitative conver-
3	2.47	1654		sion; 70–75% dimers and trimers.
				50% propylene
4	0.613	312		An increase in the unsaturates
5	1.0	458	44–48	content of the polymerizate was
6	2.0	1000	gas	obtained at low space rates
7	2.7	1000	removal	(Expt. No. 4); conversion was
			18–20%	quantitative in Expts. 4–6; 80%
			C_3H_6	conversion in Expts. Nos. 7–8.
8	3.2	1265		
				25% propylene
9	0.410	62	} 52	Content of unsaturates increased during prolonged operation; no
10	0.328	62		aromatic hydrocarbons.
				50% propylene; experiments at 150°
11	0.668	375	} 40–45	Unsaturates content increased
12	0.700	292		with an increase in the time on the catalyst; the catalyst grad- ually increased in volume and lost compressive strength.

degree of branching of the polymers obtained under conditions leading to 1) trimer and 2) tetramer, the nonane fractions boiling in the range of 130 to 140° were separated into 1° fractions, and the contents of methyl and methylene groups in these fractions were determined by infrared spectroscopy using the CH group absorption band in the 3.3 μ region. In the first case, the average CH_3-group content was 5 and the CH_2-group content was 2; in the second case, the CH_3-group content was 4 and the CH_2-group content was 3; i. e., in this case, the degree of branching of the nonanes decreased somewhat with an increase in the contact time. The correctness of this conclusion was confirmed by determination of the octane numbers, which were found to be 91.5 and 86.7. We previously arrived at this same conclusion relative to the occurrence of so-called reverse isomerization, leading to a decrease in the degree of branching under conditions of prolonged contacting, the conclusion being based on oxidation of the nonenes obtained under different conditions. In the first case, nonenes having the structure (after

hydrogenation):

$$-CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3,$$

i. e., with a ratio of CH_3 to CH_2 of 5/2, were identified; in the second case, the hydrogenated products had the structure

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{C}{|}}{CH}}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3,$$
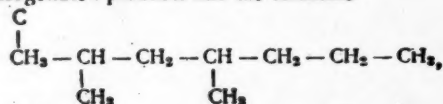
i. e., with a ratio of CH_3 to CH_2 of 4/3.

EXPERIMENTAL

Of the large number of experiments which were carried out, the experiments presented in Table 1 were conducted without recycle, with propylene concentrations in the feed of 83%, 50%, and 25%, and at various space rates; the pressure was constant (at 60–80 atm), as was the temperature, 200° (with the exception of two experiments, which were carried out at 150°). In these experiments, coke deposition and the formation of saturated

hydrocarbons did not occur, even during prolonged use of the catalyst (over 500 hours with constant polymerizate yield). Upon more detailed consideration of the data, it may be seen that experiments at rather high space rates (2.0-3.0), both with 83% and with 50% propylene in the feed, gave high yields of polymerizate. Further, it is not difficult to discern that in experiments with 83% propylene, in spite of the decreased content of tetramers and pentamers (25-30%) in this case, the over-all yield of the desired fraction was rather high owing to the higher over-all yield of polymerizate. This feed composition is particularly valuable when there is a demand for dimer and trimer. When 50% propylene was polymerized at space rates of 2.0-3.0, the yield of tetramer and pentamer was a maximum and reached 50%. At low space rates (0.4-0.6) and prolonged catalyst operation (150 hours and more), there was a gradual increase in the content of saturated hydrocarbons, particularly in the chief fractions of the polymerizate, accompanied by carbon deposition on the catalyst. It is interesting that a decrease in the temperature to 150° (at a space rate of 0.7) did not eliminate the increase in the content of saturated hydrocarbons. Moreover, the catalyst swelled rapidly and spalled readily at this lower temperature. Favorable results were not obtained when the temperature was increased to 250°. Thus, the optimum temperature is 175-200°, and the optimum space rate is 2 to 3 (both for 83% and for 50% propylene). We were unable to carry out experiments with mixtures of propylene with dimer and trimer fractions in our apparatus. When propylene trimer alone was fed at 220°, there was a 25% increase in the yield of tetramer (during a single pass). When a fresh feed consisting of 50% propylene and 50% propane was polymerized in the new IOR apparatus at 177-224° and a pressure of 50 atm, the yield of polymerizate was 1.5 liters per kg of catalyst per hour, while the concentration of dodecylene fraction in the polymerizate was 80% when recycling was practiced [3].

The infrared spectra were taken by B. V. Lopatin in the laboratory of the Institute of Organic Chemistry.

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2-ETHYLENIMINO-2-PHENYL-1,3-INDANEDIONE

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Over the past several years, we have studied amino derivatives of 2-substituted 1, 3-indanediones [1-5]. These compounds are of interest not only from a theoretical point of view, but also many of them exhibit clearly expressed physiological effects [6]. In a continuation of this work, we set ourselves the goal of introducing an ethylenimino group into the indanedione molecule. β-Diketones with an ethylenimino group in the active methylene group have not been described up to the present.

The interaction of 2-bromo-2-phenyl-1, 3-indanedione (I) with ethylenimine in ether solution proceeds readily at ordinary temperatures, and 2-ethylenimino-2-phenyl-1, 3-indanedione (II) is formed. In order to conserve the more valuable ethylenimine, triethylamine may be used to tie up the hydrogen bromide [7].
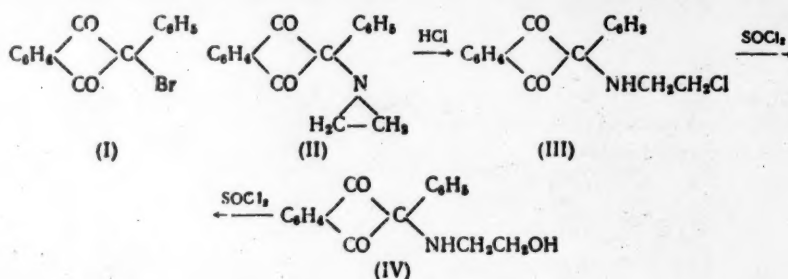
2-Ethylenimino-2-phenyl-1, 3-indanedione is a greenish yellow crystalline substance, readily soluble in organic solvents. When a solution of it in absolute ether was saturated with hydrogen chloride, a white salt-like precipitate was formed; this proved to be the hydrochloride of 2-β-chloroethylamino-2-phenyl-1, 3-indanedione (III), which was formed by opening of the ethylenimine ring by the hydrogen chloride. Hydrogen bromide and hydrogen iodide act in a similar manner. The ease with which the ethylenimine ring is opened by hydrogen halide has repeatedly been pointed out in the literature [8, 9]. It takes place in aqueous solutions [7, 10, 11]. M. Yu. Lidak, S. A. Giller and A. Ya. Medne [7] proposed that the ethylenimine ring is cleaved by the acid in the presence of traces of water; our experiment showed that cleavage of the ring by hydrogen halide also takes place in an anhydrous medium.

That structure (III) is correct was proved by synthesis of the previously described [2] 2-β-hydroxyethylamino-2-phenyl-1, 3-indanedione (IV), which, by the action of thionyl chloride, was converted to (III). Like other compounds containing a secondary amino group, it formed the corresponding nitroso and acetyl derivatives.

EXPERIMENTAL

2-Ethylenimino-2-phenyl-1, 3-indanedione (II). a) A solution of 4 ml of ethylenimine in absolute ether was added to a solution of 10 g of 2-bromo-2-phenyl-1, 3-indanedione in absolute ether. On the following day, the resulting very hygroscopic, white precipitate was separated, and the filtrate was evaporated under vacuum. A greenish yellow crystalline precipitate formed, and this was purified by recrystallization from absolute ether. The yield was 6.3 g (72.5%). The m. p. was 109-110°.

(b) To a solution of 5 g of 2-bromo-2-phenyl-1, 3-indanedione in absolute ether was added a solution of 1 ml of ethylenimine and 1.8 ml of triethylamine in ether. Triethylamine hydrobromide separated as a white precipitate (m. p. 248°). Further treatment was as in a). The yield was 3.5 g (80%). The m. p. was 109-110°.

A mixture of this material with the substance prepared by method a) melted without depression of the melting point.

$$\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}. \quad \begin{array}{l} \text{Found \%:N} \quad 5.59 \\ \text{Calculated \%:N} \quad 5.32. \end{array}$$

Opening of the ethylenimine ring in 2-ethylenimino-2-phenyl-1, 3-indanedione. 1) By hydrogen chloride. Unrecrystallized (II), prepared by method a) from 15 g of (I) and 5.5 ml of ethylenimine, was dissolved in a mixture of absolute ether and dioxane (3:1), and the solution was saturated with dry HCl. The resulting white precipitate, 16.5 g (98.3%), was recrystallized from absolute alcohol containing ether, and 14 g (83.5%) of 2-β-chloroethylamino-2-phenyl-1, 3-indanedione hydrochloride was obtained. The m. p. was 218-220° (with decomposition).

$$\text{C}_{17}\text{H}_{14}\text{O}_2\text{NCl} \cdot \text{HCl}. \begin{array}{l} \text{Found \%: N} \quad 4.02; \ 4.23 \\ \text{Calculated \%: N} \quad 4.17. \end{array}$$

A 5% solution of soda was poured over 7 g of this salt, and the resulting base was extracted with ether. The ether solution was dried with anhydrous sodium sulfate and evaporated under vacuum. The oily residue crystallized on standing. The coarse yellow crystals of (III) melted at 58-60°. The yield was 4.5 g (72%). The compound was readily soluble in organic solvents.

$$\text{C}_{17}\text{H}_{14}\text{O}_2\text{NCl}. \begin{array}{l} \text{Found \%: N} \quad 4.56 \\ \text{Calculated \%:N} \quad 4.67. \end{array}$$

2) By hydrogen bromide. A solution of 2 g of (II) in absolute ether was saturated with hydrogen bromide. On the following day, the resulting white precipitate of 2-β-bromoethylamino-2-phenyl-1, 3-indanedione hydrobromide (3.2 g, 99%, m. p. 223° with decomposition) was separated and recrystallized from alcohol by the addition of ether. The yield was 3 g (93%, m. p. 223° with decomposition). The substance was difficultly soluble in alcohol, and was hydrolyzed by water.

$$\text{C}_{17}\text{H}_{14}\text{O}_2\text{NBr} \cdot \text{HBr}. \begin{array}{l} \text{Found \%: N} \quad 3.24 \\ \text{Calculated \%: N} \quad 3.30. \end{array}$$

Treatment of the salt with a solution of soda in a manner similar to that described above gave the free base. The coarse yellow crystals of 2-β-bromoethylamino-2-phenyl-1, 3-indanedione melted at 58-60° (from ether).

$$\text{C}_{17}\text{H}_{14}\text{O}_2\text{NBr}. \begin{array}{l} \text{Found \%:N} \quad 4.05 \\ \text{Calculated \%:N} \quad 4.07. \end{array}$$

A solution of 0.8 g of the base in ether was saturated with dry HCl. The resulting 2-β-bromoethylamino-2-phenyl-1, 3-indanedione hydrochloride was recrystallized from absolute alcohol by the addition of absolute ether. The yield was 0.75 g (83.3%, m. p. 211-213° with decomposition). It hydrolyzed when dissolved in water.

$$\text{C}_{17}\text{H}_{14}\text{O}_2\text{NBr} \cdot \text{HCl}. \begin{array}{l} \text{Found \%: N} \quad 3.86 \\ \text{Calculated \%: N} \quad 3.68. \end{array}$$

3) By hydrogen iodide. 5.3 g of (II) was suspended in 10 ml of dry dioxane, and 8 ml of concentrated hydriodic acid was added. The precipitate dissolved with the evolution of heat, and a white precipitate formed when the solution was cooled. The precipitate was washed with a mixture of alcohol and ether (1:2). The yield was 8.7 g (82.7%, m. p. 182-184° with decomposition). Recrystallization from absolute alcohol containing ether resulted in 7.3 g (69.5%) of white crystals of 2-β-iodoethylamino-2-phenyl-1, 3-indanedione hydriodide, m. p. 183-184° (with decomposition). The crystals yellowed on standing in air.

$C_{17}H_{14}O_2NI$ III Found %N 2,42
Calculated %N 2,69.

The salt was treated with a soda solution in the manner described above, and 2-β-iodoethylamino-2-phenyl-1, 3-indanedione was obtained in the form of coarse yellow crystals; the yield was 80%. The m. p. was 58-60° (from ether).

$C_{17}H_{14}O_2HI$ Calculated Found %: N 3,54
%: N 3,59.

A solution of 0.8 g of this base in ether was saturated with dry HCl, and 0.8 g (91.4%) of 2-β-iodoethyl-amino-2-phenyl-1, 3-indanedione hydrochloride was obtained. The white crystals were recrystallized from absolute alcohol + ether. The m. p. was 188° (with decomposition). The substance was hydrolyzed by water.

$C_{17}H_{14}O_2NI$ HCl. Calculated %: Found %: N 3,00
N 3,28.

2-β-Chloroethylamino-2-phenyl-1, 3-indanedione hydrochloride. a) 6 ml of thionyl chloride was added to 6 g of 2-β-hydroxyethylamino-2-phenyl-1, 3-indanedione in 20 ml of dry dichloroethane, and the mixture was refluxed. Everthing crystallized at first (the salt of (IV) was formed, m. p. 207°), but the crystals later went into solution. The mixture was heated for 3 hours, and the excess thionyl chloride and dichloroethane were distilled under vacuum. The oil which separated soon crystallized. The residual traces of thionyl chloride were decomposed by the addition of several milliliters of methanol, the mixture was again evaporated under vacuum, and the precipitate was washed with absolute ether. The yield was 6.3 g (99%) of fine white crystals, m. p. 218-220° (with decomposition). After recrystallization from absolute alcohol containing ether, the crystals melted at 218-220°. The substance was comparatively difficultly soluble in methanol and ethanol. It was hydrolyzed by water, the yellow base being precipitated.

b) 5 ml of thionyl chloride was poured over 0.5 g of (IV). The precipitate first dissolved, and then everything crystallized. Further treatment was by the method described under a). The yield was 0.5 g (94.5%), m. p. 218-220° (with decomposition; from alcohol + ether). A mixture of this compound with the preceding melted without depression of the melting point.

$C_{17}H_{14}O_2NCl$·HCl. Calculated %: Found %: N 4,26 (a); 4,07 (b)
N 4,17.

1 g of this salt was ground with 2.5% ammonia, and the resulting oil was washed with water. The yellow oil solidified on standing. The yield was 0.8 g (89.8%). Recrystallization from dilute alcohol resulted in 0.6 g (67.3%) of greenish yellow crystals of base (III), m. p. 58-60°.

$C_{17}H_{14}O_2NCl$. Calculated %: Found %: N 4,81; 4,50
N 4,67.

Nitroso derivative. An excess of sodium nitrite was added to a solution of 2-β-chloroethylamino-2-phenyl-1, 3-indanedione hydrochloride (hydrochloride of III) in dilute acetic acid. Dilution of the solution with water precipitated 0.5 g (91%) of the nitroso derivative. Crystallization from alcohol gave 0.45 g (81.7%) of fine white crystals of 2-N-nitroso-β-chloroethylamino-2-phenyl-1, 3-indanedione, m. p. 150-151°.

$C_{17}H_{13}O_3N_2Cl$. Calculated %: Found %: N 8,47
N 8,50.

Acetyl derivative. 5 ml of a mixture of acetic anhydride and acetyl chloride was poured over 0.5 g of the hydrochloride of (III), and the mixture was refluxed until the resulting precipitate again went into solution. The solution was poured into water, and 0.5 g (87.7%) of a white precipitate was obtained. Recrystallization from alcohol gave 0.4 g (70.2%) of 2-N-acetyl-β-chloroethylamino-2-phenyl-1, 3-indanedione, m. p. 170-171°.

Found %: N 4.31
$C_{16}H_{16}O_3N$. Calculated %: N 4.10.

We should like to express our appreciation to M. Lidak for the gift of the ethylenimine.

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STEREOCHEMICAL STUDY OF THE ACTIVE CENTERS
OF A CATALYST

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The study of catalytic reactions of molecules having a complex configuration permits conclusions as to the microstructure of the catalytically active surface of the catalyst. This may be seen from the following. According to multiplet theory, the reacting part of the molecule must be oriented toward the active surface of the catalyst. In order for the reaction to proceed, the remaining (extra-index) part of the molecule must be arranged around the active center. For this requirement to be satisfied, the surface must have the appropriate microrelief, since in a given case the extra-index part of the molecule has a complex steric structure which, owing to the inflexibility of the structure, excludes free rotation. For a given type of three-point adsorption of projecting substituents attached to the reacting atoms in the index group (when only stereospecific adsorption is possible [1]), the height and extent of the catalytically active surface of an active center on the surface of a catalyst are determined by the dimensions of these groups. By varying the dimensions and structure of the reacting molecules, it is possible to determine the real dimensions of the projecting centers of the catalytically active surface and their statistical distribution.

From this point of view, the hydrogenation of a derivative of triptycene, 2, 3-(anthrylene-9', 10')-5, 6-(anthrylene-9", 10")-2-cyclohexene-1, 4-dione (I), appeared to be of interest inasmuch as the steric configuration of this compound is still more complex than those of the triptycene derivatives studied earlier [2].
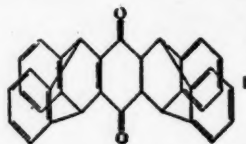
Compound (I) was synthesized by condensation of triptycenequinone (II) with anthracene by refluxing equimolar amounts of these substances in dry ethylbenzene for 5 hours.
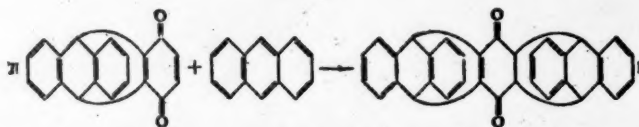
The reaction mixture was cooled, and the product was filtered, washed with toluene for the removal of unreacted triptycenequinone, and recrystallized from a toluene—dioxane mixture (1:2). Compound (I) was obtained in the form of yellow crystals with an m. p. of 268° (with decomposition).

	Found %:	C 88.17;	H 4.72
$C_{24}H_{22}O_3$.	Calculated%:	C 88.31;	H 4.76

Compound (I) did not form a dinitrophenylhydrazone, apparently as a consequence of steric hindrance. In previous work, we were able to prepare only the monohydrazones of less complex derivatives of triptycene containing two carbonyl groups [2]. Like all of the previously studied triptycene derivatives, compound (I) did not exhibit the luminescence characteristic of anthracene derivatives. On storage in air, compound (I) gradually changed, apparently being converted to the hydroquinone (III) with an m. p. of 366°.
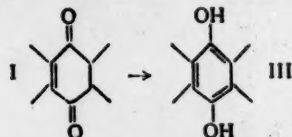
The hydrogenation of compound (I) was carried out in a thermostatted rocking bomb (TS-17 thermostat) at 600 oscillations per minute; the reaction was conducted at atmospheric pressure and 45° over a skeletal nickel catalyst in a medium of freshly distilled and peroxide-free dioxane. The course of the reaction can be represented by the following scheme:

Figure 1 shows the variation in the rate of hydrogenation of compound (I) (ml H_2 S. T. P. per minute) with the degree of conversion (in %). For comparison, Fig. 1 also shows a curve for the hydrogenation of triptycenequinone under the same conditions. It can be seen that hydrogenation of compound (I) does take place under the conditions used; however, the rate was somewhat lower than in the case of triptycenequinone, the molecules of which do not have such a complex steric structure.
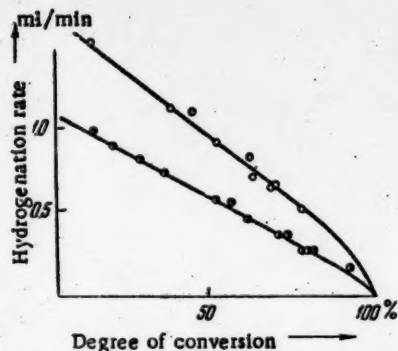
Fig. 1. Hydrogenation of dianthrylene-dihydrobenzoquinone. Variation of hydrogenation rate (in ml H_2 (S. T. P.) per minute) with degree of conversion (%) of dianthrylenedihydrobenzoquinone (lower curve) and triptycenequinone (upper curve).

After completion of the reaction (absorption of one mole of hydrogen), the reaction mixture was filtered free of catalyst, and the hydrogenation product (IV), colorless crystals, was recrystallized from dioxane; m. p. 221° (with decomposition).

	Found %	C 87.19;	H 5.57
$C_{74}H_{24}O_2$.	Calculated %	C 87.93;	H 5.17

The investigation of the structures of compounds (I) and (IV) was attended by the well-known difficulties. Both compounds were difficultly soluble in all organic solvents and were difficult to purify by recrystallization or chromatography. This apparently explains the deviations of the analytical data from the calculated; analysis of the products obtained from different experiments gave somewhat divergent results, the averages of which are presented above. Owing to steric hindrance, compounds (I) and (IV) did not form derivatives at their functional groups. The infrared spectra* of compounds (I) and (IV) showed the presence of an ethylenic bond in compound (I) and its absence in the hydrogenation product (IV). Moreover, frequencies characteristic of O−H bonds were not present in the spectrum of compound (IV), which indicates that isomerization of (IV) to the dienol (V) did not occur.

* The authors express their appreciation to Yu. P. Egorov for taking the i. r. spectra.
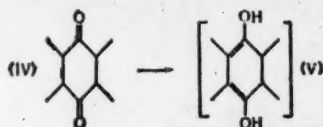
Apparently, hydrogenation of compound (I) without the formation of by-products leads to the dihydro diketone (IV). The disposition of the molecule of compound (I) on the surface of the catalyst is shown schematically in Fig. 2.

It is evident that only a planar orientation of the cyclohexendione ring on the surface of the catalyst is possible during the hydrogenation of this compound. From the actual dimensions of the model of the active complex may be determined the height of the active center of the surface – the center on which hydrogenation of compound (I) proceeds. The fact that the reaction does take place, although it proceeds at a low rate, indicates that the height of the active center cannot be less than 3.17 A, since otherwise there could not be a planar superposition of the reacting molecule on the catalyst surface, which is required for occurrence of the reaction. The distance between the meso positions on the model (see Fig. 2) permits an approximate evaluation of the dimensions of the surface of the active center; these dimensions cannot be greater than 4.8 A, since if they were, superposition of the molecule on the active center would be impossible, and, consequently, the reaction would not take place.
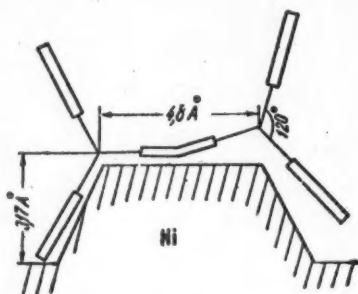
Fig. 2. Stereochemical model of the intermediate complex in the hydrogenation of dianthrylenedihydrobenzoquinone on a nickel catalyst.

This stereochemical model of the intermediate complex differs substantially from that in the previously studied hydrogenation of triptycenequinone; in that case, the reaction proceeded by an edge mechanism, and the dimensions along the sides of the substituents played a smaller role. In the present case, the form and disposition of the extra-index substituents have, as in enzyme catalysis, an especially great significance. As a consequence of the planar orientation of the molecules and the steric hindrance during the reaction, the number of active centers on which hydrogenation can take place is considerably reduced. Therefore, the reaction rate is lower than the rate of hydrogenation of the triptycene derivatives previously studied by us.

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*Original Russian pagination. See C. B. translation.

A STUDY OF THE OXIDATION OF TiCl₃ WITH ISOPROPYLBENZENE HYDROPEROXIDE IN AQUEOUS AND HYDROCARBON MEDIA

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Insoluble catalytic complexes formed by the interaction of organometallic compounds with titanium tetrachloride contain reduced titanium salts, chiefly Ti^{3+}, which are readily oxidized to Ti^{4+}. The oxidation of Fe^{2+} to Fe^{3+} by the action of hydroperoxides is widely used at present for the initiation of radical processes, particularly polymerization processes. The oxidation of hydrocarbon-soluble Fe^{2+} salts by oxygen leads, at ordinary temperatures, to the development of chain oxidative processes, particularly destruction or cross-linking of polymers [1]. Similar phenomena are also to be expected in polymers containing Ti^{3+}. In connection with this, there has arisen the problem of studying the oxidation of Ti^{3+} to Ti^{4+} without the complication of side processes leading to deterioration of the structure and properties of the polymers.
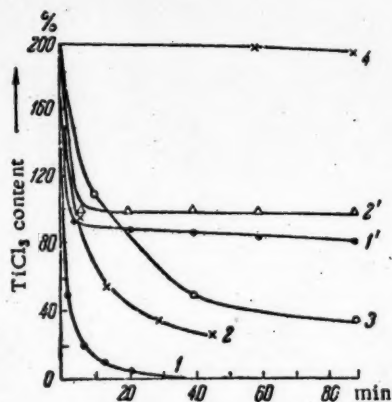
Fig. 1. Interaction of TiCl₃ with cumene hydroperoxide in water and water-alcohol solution. Ratio TiCl₃ to hydroperoxide = 2:1 (mole). In the absence of acrylonitrile: 1—at 20°, 2—at 0°, 3—at 20°, 4—at—70°; in the presence of a rylonitrile: 1'—at 20°, 2'—at 0°.

For our study, we selected the oxidation of TiCl₃ by cumene hydroperoxide in aqueous and hydrocarbon solutions. The study of this reaction in dilute aqueous solutions (0.05% hydroperoxide solution) at various temperatures showed that 1 mole of hydroperoxide consumed 2 moles of TiCl₃ (Fig. 1). In the presence of free radical acceptors (acrylonitrile, methyl methacrylate), the ratio of reacting TiCl₃ to hydroperoxide approached 1 (Fig. 1, 1 and 2). The reaction proceeds at an appreciable rate even at very low temperatures, but practically stops at a temperature of about—70°. Methane, in an amount of 15-17% of the original hydroperoxide, is evolved during the reaction at a temperature of 20° and with a comparatively high concentration of reacting components (1% hydroperoxide solution). In the presence of the free radical acceptors indicated above, the formation of methane was completely suppressed. During the study of the products formed by the interaction of TiCl₃ and hydroperoxide in a ratio of 2:1 (mole) in aqueous solution at 20°, it was established that the major products of hydroperoxide decomposition are dimethylphenylcarbinol (yield, 65-75% of theoretical) and acetophenone (15-17% of theoretical). TiO₂ separated quantitatively from the aqueous solution on standing. On the basis of the data which have been presented, it can be assumed that the following processes take place in aqueous solutions:

$$\text{C}_6\text{H}_5 - \overset{\overset{\displaystyle \text{CH}_3}{|}}{\underset{\underset{\displaystyle \text{CH}_3}{|}}{\text{C}}} - \text{OOH} + \text{TiCl}_3 \rightarrow \text{C}_6\text{H}_5 - \overset{\overset{\displaystyle \text{CH}_3}{|}}{\underset{\underset{\displaystyle \text{CH}_3}{|}}{\text{C}}} - \text{O}^\cdot + \text{HOTiCl}_3; \tag{1}$$

$$\text{C}_6\text{H}_5 - \overset{\overset{\displaystyle \text{CH}_3}{|}}{\underset{\underset{\displaystyle \text{CH}_3}{|}}{\text{C}}} - \text{O}^\cdot + \text{TiCl}_3 \rightarrow \text{C}_6\text{H}_5 - \overset{\overset{\displaystyle \text{CH}_3}{|}}{\underset{\underset{\displaystyle \text{CH}_3}{|}}{\text{C}}} - \text{OTiCl}_3 \xrightarrow{\text{HOH}} \text{C}_6\text{H}_5 - \overset{\overset{\displaystyle \text{CH}_3}{|}}{\underset{\underset{\displaystyle \text{CH}_3}{|}}{\text{C}}} - \text{OH} + \text{HOTiCl}_3; \tag{2}$$

$$\text{C}_6\text{H}_5 - \overset{\overset{\displaystyle \text{CH}_3}{|}}{\underset{\underset{\displaystyle \text{CH}_3}{|}}{\text{C}}} - \text{O}^\cdot \rightarrow \text{C}_6\text{H}_5\text{COCH}_3 + \text{CH}_3^\cdot \rightarrow \text{CH}_4; \tag{3}$$

$$\text{HOTiCl}_3 \xrightarrow{\text{HOH}} \text{TiO}_2. \tag{4}$$
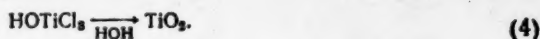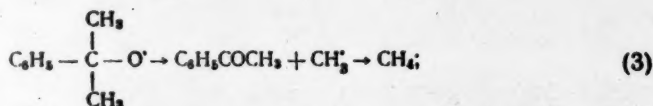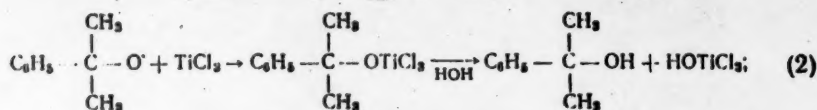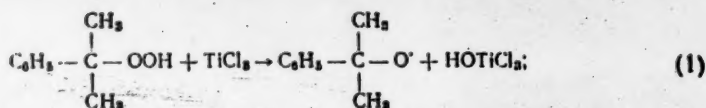
Reactions 2 and 3 are suppressed in the presence of free radical acceptors.

The reaction between TiCl_3 and cumene hydroperoxide can be used to initiate emulsion polymerization processes at temperatures down to $-50°$, and may also be used for solution polymerization of partially water-soluble monomers (acrylonitrile, methyl methacrylate) at low temperatures. The yields of polystyrene in an emulsion system after 4 hours reaction time are: at $-18°$, 50% of theoretical; at $-50°$, 13% of theoretical. In a homogenous aqueous solution, the yield of polyacrylonitrile is 60% of theoretical after 1 hour.

Hydroperoxide and TiCl_3 react in a ratio of close to 1 in a hydrocarbon medium (a mixture of benzene with 8-10% absolute ethyl alcohol).

TABLE 1

Interaction of TiCl_3 with Cumene Hydroperoxide in a Hydrocarbon Medium in the Presence of a-Methylstyrene (300 Moles per Mole of Hydroperoxide) at $20°$

Initial TiCl_3:hydroperoxide (mole)	1:1	2:1	1:2
TiCl_3 found (% of initial)	9.2	53.2	0
Hydroperoxide	0	0	44
TiCl_3:hydroperoxide reacted (mole)	0.91:1	0.94:1	0.88:1

In hydrocarbon solutions, the role of Reaction 2 is less owing to the development of the chain transfer reaction: $\text{RO} + \text{AH} - \text{ROH} + \text{A}$ ($\text{AH} -$ solvent). It may be assumed that Reaction 2 is specific only for radicals of the type RO (HO). An analogous reaction with R would lead to a very unstable organometallic compound. In hydrocarbon solution, the interaction of TiCl_3 with hydroperoxide takes place practically instantaneously. As a result of this, as in Fe^{2+}-hydroperoxide systems, this reaction cannot be used in hydrocarbon media for the initiation of long-chain processes, for example, polymerization processes. However, for processes in which the reaction chains are short, for example, rubber cross-linking, the system TiCl_3-hydroperoxide is very effective. The oxidation of TiCl_3 by hydroperoxide at $20°$ brings about immediate cross-linking in 2% solutions of polybutadiene and polyisoprene in benzene.

Cross-linking processes in rubbers initiated by oxidation of TiCl_3 with hydroperoxide, like the similar initiation of polymerization in aqueous media, can be suppressed by the use of a number of inhibitors of radical processes. The inhibiting action of hydroquinone and quinone, aromatic nitro derivatives, p-phenylenediamine, and phenyl-β-naphthylamine (Neozone D) on the cross-linking of rubbers was studied.

It follows from the data presented that aromatic nitro derivatives and phenyl-β-naphthylamine are quite effective inhibitors of cross-linking in rubbers during oxidation of TiCl_3 by hydroperoxide. The decreased activity of quinone is evidently due to the fact that its action is specific for acid media. The strong inhibiting effect

TABLE 2

Inhibition of Rubber Cross-Linking During Oxidation of TiCl$_3$ with Cumene Hydroperoxide. TiCl$_3$:hydroperoxide = 1; hydroperoxide concentration 5 wt. % of the polymer; polymer concentration in the solution, 2%; temperature, 20°

Rubber	Inhibitor	Effective inhibitor concn. (mole % of hydroperoxide)	Effect
Polybutadiene	Without inhibitor	—	Instantaneous cross-linking (gel)
	Benzoquinone	100	Vis. of soln. did not change
	Nitrobenzene	25	Same
	Dinitrobenzene	25	Same
	Neozone D	25	Same
Polyisoprene	Without inhibitor	—	Instantaneous cross-linking (gel)
	Benzoquinone	100	Vis. of soln. did not change
	Nitrobenzene	50	Same
	Dinitrobenzene	50	Same
	Neozone D	50	Same

of phenyl-β-naphthylamine is connected with the presence in the system of RO radicals which bring about the removal of an H atom from the NH group. As is well known, phenyl-β-naphthylamine does not inhibit processes involving the participation of aliphatic or aromatic radicals [2].

From the data presented above, it follows that oxidation of Ti^{3+} salts by cumene hydroperoxide takes place with the development of radical chain reactions which, in aqueous media, can initiate a polymerization process and which, in hydrocarbon media, lead to cross-linking of rubbers. The development of these processes can be suppressed by specific inhibitors.

Thus, in systems containing rubber solutions and Ti^{3+} salts, the latter can be easily converted to Ti^{4+} salts by the action of the appropriate amounts of hydroperoxide in the presence of inhibitors without the development of secondary radical processes.

EXPERIMENTAL

The system TiCl$_3$—cumene hydroperoxide in aqueous solutions. For this work, aqueous hydrochloric acid solutions of TiCl$_3$ (15.2%; GOST 311—41) and a solution of the hydroperoxide in water freed from dissolved air were used. Determination of the hydroperoxide concentration was carried out iodometrically [3]. The TiCl$_3$ was determined by titration of a solution of ferric ammonium sulfate in the presence of ammonium thiocyanate. The acetophenone and dimethylphenylcarbinol were extracted from the reaction mixture with cumene, and were determined by the well-known method [4].

The emulsion polymerization was carried out at a pH of 3 using Nekal (an Na alkylnaphthalene sulfonate) as the emulsifier and alcohol, glycerin, or ethylene glycol as an anti-freeze. The ratio of TiCl$_3$ to hydroperoxide was 2:1, and the hydroperoxide concentration was 0.5% of the monomer.

The system TiCl$_3$—hydroperoxide in hydrocarbon medium. 1-2% solutions of TiCl$_3$ in absolute alcohol acidified with glacial acetic acid and solutions of hydroperoxide, polymers, and inhibitors in benzene were used in this

work. When the components of the system were mixed, a solution of rubber in benzene containing 8-10% ethyl alcohol was formed. Under these conditions and with slow introduction of the alcoholic solution of $TiCl_3$ and with vigorous stirring, the rubber did not precipitate from the solution. The $TiCl_3$ precipitated from the solution as a colloidal suspension (the solution clearly showed Tyndall cone). The work studying the cross-linking action of the $TiCl_3$–hydroperoxide system was carried out using special ampoule–viscosimeters under conditions excluding traces of air and moisture [5].

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•Original Russian pagination. See C. B. translation.

METALLATION OF POLYMERS

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In investigations of the structure of polymers (or copolymers), processes which introduce metal atoms into the polymers can play a distinct role in changing polymer properties, which is one approach to the problem. Though we have been occupied with a systematic study of the question of metallation of polymers by means of organoalkali metal compounds or salts of heavy metals, we shall confine ourselves in the present paper to a description of certain mercuration and thallilation reactions.

In describing a thallilation method using trivalent thallium salts of organic acids [1], a method previously discovered by us, we pointed out the particular ease with which the thiophene ring may be thallilated. Thus, thallilation, like mercuration, of poly-α-vinylthiophene is very practicable.

On the other hand, the selection of polyvinylthiophene was dictated by the fact that the metal atom enters the polymer in a specific position (in the α-position). Metallation of polymers encounters special difficulties, because the higher polymers are solid substances, and their metallation in solution is limited to those solvents which, while possessing solvent action, are not rapidly metallated or which do not react with the metallating agent for one reason or another.

The following systems were investigated in the present work: 1) thallilation of polyvinylthiophene* (benzene medium), 2) mercuration of polyvinylthiophene (benzene medium), and 3) mercuration of polystyrene (nitrobenzene medium)**.

The selection of reaction conditions and solvent was determined by the requirement of carrying out the reaction at a moderate temperature and in a homogeneous medium. The metallating agents, thallium triisobutyrate, as well as the polymers used were readily soluble in the solvents selected. Thallilation of polyvinylthiophene in benzene solution required 15 minutes when the reaction mixture was heated on a water bath.

$$\left[\begin{array}{c} -CH-CH_2- \\ \end{array} \right]_x + x\,Tl(OOCR)_3\,x \rightarrow \left[\begin{array}{c} -CH-CH_2- \\ \end{array} \right]_x + x\,RCOOH. \tag{1}$$
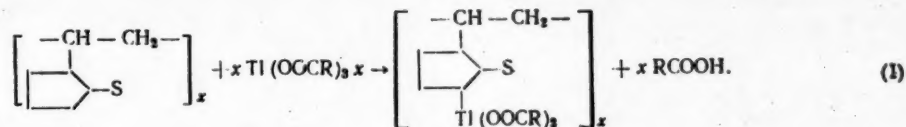
As we have shown previously [1], benzene undergoes practically no reaction under these conditions. Analysis of the reaction product indicated that the number of thallium atoms per vinylthiophene unit was 0.94–1.0.

Mercuration of polyvinylthiophene proceeds under similarly mild conditions (several minutes after the warm solutions were mixed) according to an analogous equation***:

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* Poly-α-vinylthiophene throughout this paper.

** We also successfully metallated polyvinylfuran (in the α-position).

*** In a sense, the reaction is reminiscent of the well-known method of preparing thiophene-free benzene. In copolymers of vinylthiophene and styrene, this selectivity would probably begin to appear at the end of the polymer chain.

$$\left[\begin{array}{c} -CH-CH_2- \\ | \\ \boxed{}-S \end{array}\right]_x + x\,Hg\,(OOCR)_2 \rightarrow \left[\begin{array}{c} -CH-CH_2- \\ | \\ \boxed{}-S \\ | \\ HgOOCR \end{array}\right]_x + x\,RCOOH \tag{II}$$
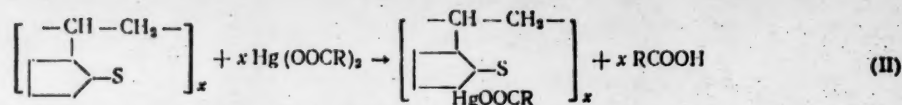
Analysis of the mercurized polyvinylthiophene indicated that one atom of mercury was introduced per vinylthiophene unit (1 : 1).

Thallilated and mercurated polyvinylthiophene are very slightly yellow powders, which are insoluble in benzene and other organic solvents; consequently, they can readily be washed free of excess metallating agent or traces of the original polymer.

Poly-α-vinylthiophene also undergoes lithiation readily; subsequent carbonation of the metallated product brings it completely into solution (I. M. Viktorova). The lithium derivative is reduced by titanium tetrachloride. The possibility of using the resulting mixture as a catalyst for the polymerization of unsaturated compounds has been investigated (O. A. Paleev). Mercuration of polystyrene is considerably more difficult, and the selection of the solvent and experimental conditions is also considerably more difficult. As a matter of fact, the media in which the mercuration can be carried out (for example, alcohol, water, acetic acid) have the disadvantage that polystyrene is not very soluble in them, while aromatic hydrocarbons such as benzene and toluene will themselves undergo mercuration.

The results of working under conditions such that homogeneity is difficult to attain are apparent from the experiments of Smirnov [2], for example; this investigator mercurated styrene in a medium of acetic acid. The length of the reaction time, the relatively high temperature (up to 118°), and the non-uniformity of heating led to reduction of the mercury acetate (used as the mercurating agent) during the mercuration process (precipitation of metallic mercury and monovalent mercury salts and scorching). The crude product obtained by subsequent treatment with hydrogen peroxide could not be reprecipitated and contained a total of only 50-60% of the mercury required by theory (on the basis of the introduction of one mercury atom per styrene unit).

Consequently, it was necessary to find conditions such that the work could be carried out in a homogeneous medium. Nitrobenzene is a medium in which polystyrene (including isotactic polystyrene) is soluble, especially with moderate heating. (As is well known, mercuration of nitrobenzene proceeds with considerable difficulty.)

Clear solutions of polystyrene and the mercury salt were mixed and heated for 20 hours at a temperature not exceeding that of the boiling water bath. We used a 10% excess of the mercury salt, which was subsequently easily washed from the polystyrene. The reaction mixture remained clear during the entire reaction time, but toward the end, after the temperature of the reaction mixture had been reduced to room temperature, the entire mixture congealed to a viscous, sticky mass (which was also transparent).

The product was reprecipitated from nitrobenzene solution by the addition of excess benzene or ether, and the isobutyric acid and mercury salt were then readily washed out. The resulting powder was dried under vacuum at 60°.

The product was a very slightly yellow powder, which could again be dissolved in nitrobenzene containing a small amount of isobutyric acid (an amount corresponding approximately to the amount of isobutyric acid liberated during the mercuration process).

We were able to prepare a mercurated polystyrene in which the amount of mercury corresponded to 0.96 atom per aromatic ring (0.96 : 1).

$$\left[\begin{array}{c} -CH-CH_2- \\ | \\ C_6H_5 \end{array}\right]_x + x\,Hg\,(OOCR)_2 \rightarrow \left[\begin{array}{c} -CH-CH_2- \\ | \\ C_6H_4HgOOCR \end{array}\right]_x + x\,RCOOH. \tag{III}$$
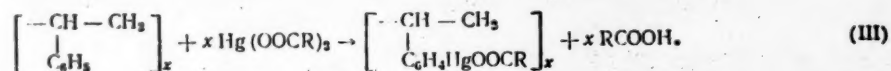
We did not determine the position into which the mercury entered (probably, chiefly the para position). The mercury atoms in the polystyrene molecule could be replaced by halogen atoms by the action of bromine.

EXPERIMENTAL

Thallium triisobutyrate, prepared as previously described by us [1], and mercury diisobutyrate, prepared from mercuric oxide and isobutyric acid, were used as metallating agents. Both isobutyrates were readily soluble in the media in which the metallation reactions were carried out (dry benzene and nitrobenzene).

Thallilation of polyvinylthiophene. The polyvinylthiophene was prepared by the benzoyl peroxide-initiated polymerization of α-vinylthiophene and subsequent reprecipitation of the polymer from benzene solution by means of methanol. The resulting precipitate was washed with methanol, and then was ground to a powder under methanol.

To a clear solution of 0.55 g (0.005 mole) of poly-a-vinylstyrene in 10 ml of benzene (thiophene-free) was added a clear solution of 2.56 g of thallium triisobutyrate in 65 ml of the same solvent. This amount of thallium salt corresponded to one molecule per vinylthiophene unit plus a 10% excess. After being heated for 3-4 minutes on a water bath, the reaction mixture became turbid, and thallilated polymer began to precipitate rapidly. The mixture was heated for 15 minutes, and, on the following day, the precipitate was washed with benzene and dried at room temperature. The yield was 1.8 g (74% of theoretical, Equation I). After additional treatment with benzene (storage under benzene for three days), the material was suction filtered, dried, and analyzed.

$$(C_4H_2SCH_2{-}CH_2)Tl[OOC \cdot CH(CH_3)_2]_2.$$ Found % Tl 39.25, 38.74 Calculated % Tl 41.89.
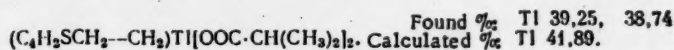
Hence, thallilation of the polyvinylthiophene was 93-94%. Thallilated poly-a-vinylthiophene is a very slightly yellow powder, which is insoluble in the usual organic solvents.

Mercuration of poly-α-vinylthiophene. To 0.55 g (0.005 mole) of poly-α-vinylthiophene in 10 ml of benzene was added 2 g (0.005 mole + 10% excess) of mercury diisobutyrate in 60 ml of the same solvent. The solutions were mixed warm. A precipitate formed after 1-2 minutes. The mixture was allowed to stand overnight to complete the reaction.

The product was suction filtered, washed with benzene, and dried at room temperature; the yield was 1.91 g — 90% of theoretical (Equation II).

$$(C_4H_2SCH{-}CH_2)HgOOCCH(CH_3)_2.$$ Found % Tl 50.52, 50.20 Calculated % Tl 50.50.
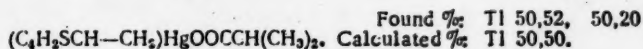
Thus, in this case there was practically quantitative introduction of mercury on the basis of one mercury atom per vinylthiophene unit (1:1). Mercurated poly-α-vinylstyrene is a very slightly yellow powder, which is insoluble in the usual organic solvents.

Mercuration of polystyrene. The polystyrene* was purified by dissolving it in benzene and pouring the solution into an excess of methanol. 2 g of the purified polystyrene was dissolved, with moderate heating, in 20 ml of dry, freshly distilled nitrobenzene (the polymer was first swelled overnight); to this completely transparent solution was added a clear solution of 7.9 g of mercury diisobutyrate in 25 ml of nitrobenzene. This amount of mercury salt corresponded to one molecule per styrene unit plus a 10% excess. Since preliminary experiments with some insufficiency of mercury salt established that during the reaction with polystyrene, a reaction for mercury ion is negative after the mixture has been heated on a boiling water bath for 19 hours, all experiments with an excess of the salt were carried out under the same conditions for 20 hours.

In contrast to the experiments in which we metallated polyvinylthiophene, a precipitate was not formed during these mercuration experiments. At the end of the heating, a viscous, homogeneous mass had been formed, and the material remained in this condition when the temperature was reduced to room temperature (indeed, the viscosity increased).

In order to separate this new polymer and to purify it, 45 ml of nitrobenzene was added to the reaction mixture, the mass was warmed slightly, and the resulting homogeneous, viscous liquid was poured into 500 ml of benzene (ether is also a good precipitant). The precipitated light yellow (almost white) substance was dried under vacuum at 60°. 4.2 g of mercurated polystyrene was obtained.

$$(CH_3)_2CHCOOHgC_4H_4 \cdot CH \cdot CH_2.$$ Found % Hg 49.33, 48.77 Calculated % Hg 51.29.

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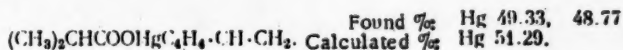
* In this case, we used commercial polystyrene produced by mass polymerization. We were also successful in mercurating isotactic polystyrene.

This corresponds to the introduction of 96% of the mercury required for one atom per styrene unit (Equation III).

Mercurated polystyrene is soluble in nitrobenzene, and is insoluble in other ordinary organic solvents.

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SYNTHESIS OF p-ISOPROPYLCYCLOHEXYLBENZENE AND ITS AUTOOXIDATION

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(Presented by Academician A. V. Topchiev, June 2, 1959)

The synthesis of p-isopropylcyclohexylbenzene (I) by cycloalkylation of isopropylbenzene with cyclohexene in the presence of $BF_3 \cdot H_3PO_4$ catalyst and its autooxidation with atmospheric oxygen were studied in the present work. With the aim of determining the optimum conditions for the synthesis of (I), the cycloalkylation of isopropylbenzene was studied at different mole ratios of reactants and catalyst in the temperature range of 20-85°. It was found that in the presence of $BF_3 \cdot H_3PO_4$, isopropylbenzene and cyclohexene react very readily with the formation of (I) as the primary product. The best conditions, under which (I) was obtained in a yield of 78% of theoretical, are: mole ratio of isopropylbenzene, cyclohexene, and catalyst, 3 : 1 : 0.3; temperature, 20-25°; and reaction time, 19 hours. Polycyclohexylisopropylbenzenes are formed in only 6% yield under these conditions. The reaction can be represented as follows:
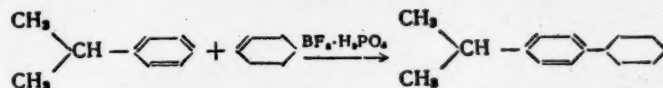
p-Isopropylcyclohexylbenzene has two tertiary carbon atoms. On the basis of the usual concepts of autooxidation of aromatic hydrocarbons, the attack of molecular oxygen should be directed at these carbon atoms first with the formation of hydroperoxides according to the scheme:
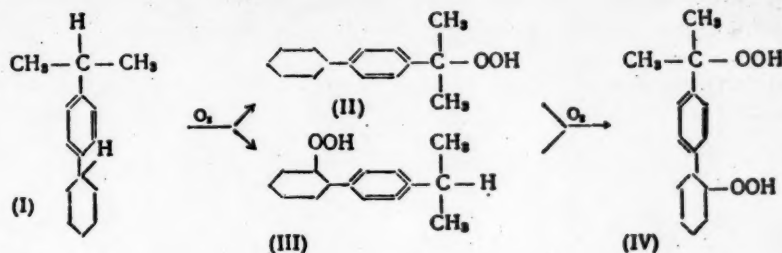
Our experiments showed that (I), prepared by cycloalkylation of isopropylbenzene with cyclohexene and prepurified by treatment with 70% H_2SO_4, is comparatively easily oxidized by atmospheric oxygen at 95-120° in the presence of manganese resinate alone or with basic promoters. In this case, the attack of the oxygen is directed chiefly at the tertiary carbon atom of the isopropyl group and ends with the formation of p-isopropylcyclohexylbenzene hydroperoxide (II). The tertiary carbon atom of the cyclohexyl radical is more difficultly oxidized by molecular oxygen under the conditions studied; therefore, cumylcyclohexylhydroperoxide (III) is formed in very small amounts.

As may be seen from the curves of Fig. 1, the autooxidation of (I) proceeds in a manner such that the hydroperoxide of (I) first accumulated in the solution up to a specific maximum, after which decomposition of the hydroperoxide begins, and its content in the solution gradually decreases. If the oxidation is continued, the hydroperoxide completely disappears from the reaction mixture, and the end products of the oxidation are p-cyclohexylacetophenone and p-cyclohexylphenol.

p-Isopropylcyclohexylbenzene (I) is oxidized considerably more slowly and to a lesser extent in the presence of manganese resinate alone than in the presence of manganese resinate and alkaline promoters. The effects of soda and calcium hydroxide as promoters are approximately the same. For example, in the presence of manganese resinate and soda, the maximum hydroperoxide content of 38% is reached after 8 hours; in the presence of manganese resinate and calcium hydroxide, the maximum hydroperoxide content of 36% is reached after 10 hours, while in the presence of manganese resinate alone a maximum of only 21% is reached under the same conditions after 18 hours. The autooxidation of (I) proceeds at its highest rate, about 6% per hour, and yields the maximum concentration of hydroperoxide, 61%, in the presence of manganese resinate, soda, and barium peroxide at 118-120° and an air feed rate of 30 liters/hour.

The rate and extent of the autooxidation depends on the temperature (Fig. 2) and also on the air feed rate. The oxidation of (I) proceeds in a peculiar manner in the presence of manganese resinate, calcium hydroxide, cobalt acetate, and sodium stearate. In this case, the maximum hydroperoxide content in the solution is 6% and is reached after 6 hours; a decrease in the concentration then begins, and the hydroperoxide disappears completely from the solution after 10 hours and does not reappear over a period of some tens of hours. The reaction products are p-cyclohexylacetophenone and p-cyclohexylphenol. Cyclohexylphenol and acetone are formed by cleavage of the hydroperoxide by concentrated sulfuric acid. Only traces of p-isopropylphenol are formed.

Fig. 1. The effect of alkaline promoters on the autooxidation of p-isopropylcyclohexylbenzene at 118-120° and an air feed rate of 30 liters/hour. 1—manganese resinate; 2—manganese resinate and soda; 3—manganese resinate and calcium hydroxide; 4—manganese resinate, soda, and barium peroxide.
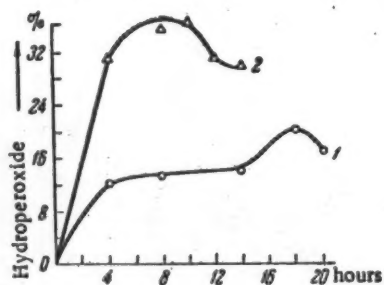
Fig. 2. Effect of temperature on the autooxidation of p-isopropylcyclohexylbenzene in the presence of manganese resinate and calcium hydroxide: 1—95-100°; 2—118-120°.

EXPERIMENTAL

Cycloalkylation of isopropylbenzene with cyclohexene. The isopropylbenzene was freshly distilled commercial product (b. p. 149-152°; d_4^{20} 0.8620; n_D^{20} 1.4910). The cyclohexene was prepared by dehydration of cyclohexanol (b. p. 81-83°; d_4^{20} 0.8102; n_D^{20} 1.4460). The reaction was carried out in a three-neck flask fitted with a mechanical stirrer. 20.5 g (0.25 mole) of cyclohexene was used for each experiment; this was mixed with $1/4$ of the calculated amount of isopropylbenzene and added to a mixture of isopropylbenzene and catalyst at a rate of 4.5 g/hour. After the addition of the entire amount of cyclohexene, the reaction mixture was stirred for an additional fixed time at the temperature of the experiment. After the appropriate treatment, the unreacted isopropylbenzene was distilled, and the cycloalkylation products were then distilled. The most characteristic experiments are reported in Table 1.

The isopropylcyclohexylbenzene fractions from all experiments were treated with 70% H_2SO_4 and stirred until the hydrocarbon was decolorized; the acid layer was then separated, and the hydrocarbon was neutralized with 5% soda solution, washed with water, dried with calcium chloride, and distilled. It was a colorless liquid; b. p. 132-134° at 10 mm; d_4^{20} 0.9301; n_4^{20} 1.5153; MR_D found, 65.46; calculated, 65.67. Heating at incipient boiling for 104 hours with 30% HNO_3 gave a 96% yield of terephthalic acid, which was characterized by conversion to its dimethyl ester. This serves as proof that the product was p-isopropylcyclohexylbenzene (I).

Autooxidation of p-isopropylcyclohexylbenzene. Oxidation of (I) was carried out with atmospheric oxygen to the formation of the maximum hydroperoxide concentration and

TABLE 1

Cycloalkylation of Isopropylbenzene with Cyclohexene

Expt. No.	Mole ratio of isopropylbenzene, cyclohexene and catalyst	Reac. Temp. °C	Obtained		high-boiling products g
			isopropylcyclohexylbenzene fraction		
			% of theoretical	boiling range °C/mm	
1	4:1:0.3	65—70	70.3	128—134°/6	1.36
2	4:1:0.2	65—70	63.6	130—137°/7	3.00
3	3:1:0.3	80—85	66.3	120—125°/3	1.46
4	3:1:0.3	60—65	71.3	120—127°/4	1.34
5	3:1:0.3	40—45	69.5	126—133°/5	—
6	3:1:0.3	20—25	70.0	110—114°/1	4.63
7	3:1:0.3	20—25	72.9	119—125°/3	1.95
8	3:1:0.3	20—25	77.7	121—126°/3	2.82
9	3:1:0.2	65—70	60.8	128—133°/5	1.94
10	3:1:0.1	65—70	60.0	135—143°/20	0.40
11	2:1:0.3	65—70	59.4	112—116°/1	2.50
12	2:1:0.2	65—70	57.4	130—138°/10	2.28
13	1:1:0.2	65—70	55.9	118—122°/2	5.70

Note: Reaction time in Experiment No. 7 was 11.5 hours, 19 hours in Experiment No. 8, and 8.5 hours in all remaining experiments.

TABLE 2

Autooxidation of p-Isopropylcyclohexylbenzene at 118-120° and an Air Feed of 30 Liters/Hour

Expt. No.	Taken for autooxidation				Max. hydroperoxide conc., %	Oxidn. time hours	Av. rate of formn. of hydroperoxide, %/hr.
	p-isopropylbenzene g	manganese resinate, mg	promoter				
			formula	mg			
1	22.5	0.4	—	—	21	18	1.2
2	26.6	0.8	Na$_2$CO$_3$	130	38	8	4.7
3	20.2	0.6	Ca(OH)$_2$	100	36	10	3.6
4*	40.5	1.2	Ca(OH)$_2$	100	20	18	1.1
5	20.2	0.8	Na$_2$CO$_3$ BaO$_2$	100 50	57	10	5.7
6	40.5	1.2	Na$_2$CO$_3$ BaO$_2$	100 50	53	12	4.4
7	60.4	2.7	Na$_2$CO$_3$ BaO$_2$	300 180	61	11	5.5
8	31.6	0.4	NaOH	470	24	17	1.4

* Experiment carried out at 95-100°.

in some experiments to the complete disappearance of hydroperoxide from the reaction mixture. The concentration of hydroperoxide was determined iodometrically every 2-4 hours.

40.5 g of (I), 1.2 mg of manganese resinate, 40 mg of cobalt acetate, 80 mg of sodium stearate, and 100 mg of calcium hydroxide were placed in a glass-column reactor in which a Schott filter was sealed, and air was passed at a rate of 5 liters/hour through the mixture at a temperature of 118-120°. The concentration of hydroperoxide in the solution was 6% after 6 hours, it had decreased to 1% after 8 hours, and after 10 hours the hydroperoxide had disappeared completely from the reaction mixture. After air had been passed through the reaction mixture for 102 hours, the mixture was treated with 10% NaOH solution, and the neutral upper layer was separated, washed with water, dried with calcium chloride, and distilled. This yielded unoxidized (I) and p-cyclohexylacetophenone with a yield of 31.2%. p-Cyclohexylphenol was obtained in 16% yield by appropriate treatment of the alkaline solution.

Air was passed at a rate of 15 liters per hour into 20.2 g of (I), 0.6 mg of manganese resinate, 50 mg of barium peroxide, and 100 mg of soda at a temperature of 118-120°. The maximum concentration of hydroperoxide, 31%, was reached in 6 hours. The per cent hydroperoxide then began to decrease, and at 26 hours, the hydroperoxide had completely disappeared from the reaction mixture. The products were distilled without preliminary treatment. This gave p-cyclohexylacetophenone and p-cyclohexylphenol in yields of 17.5% and 27.3%, respectively. Data are summarized in Table 2 for the experiments in which the oxidation of (I) was carried to the maximum concentration of hydroperoxide in the reaction mixture and was stopped when the concentration began to decrease. Hydroperoxide of 61% concentration has an n_D^{20} of 1.5288. It is a yellow liquid with a quite agreeable odor; it decomposes during distillation at 1 mm pressure.

Autooxidation of p-isopropylcyclohexylbenzene in the presence of a considerable amount of NaOH (3 g per mole of hydrocarbon) was accompanied by precipitation of the salt of the hydroperoxide from the reaction mixture as an opaque gelatinous mass.

p-Isopropylcyclohexylbenzene hydroperoxide was tested as an initiator for butadiene—styrene emulsion copolymerization. It was found that it is 2.3 times more active as an initiator than cumene hydroperoxide, which is used in industry.

TABLE 3

Cleavage of p-Isopropylcyclohexylbenzene Hydroperoxide

Expt. No.	Taken for cleavage				Reaction temp. °C	Time, hr	p-cyclohexylphenol obtained, %
	hydroperoxide sol., g	hydroperoxide concn, %	tot. hydroperoxide, g	sulfuric acid, g			
1	10	15	3.0	0.03	60—70	6	33.3
2	18	30	5.4	0.02	50—55	12	50.0
3	25	37	9.3	0.04	55—60	8	43.6
4	39	39	15.4	0.03	85—90	1	34.6
5	17	48	8.2	0.03	58—60	9	55.0

Sulfuric acid cleavage of the hydroperoxide was carried out by dropwise addition of 98% H_2SO_4 to hydroperoxide solutions of different concentrations. The temperature was maintained at not above 90°, and completion of cleavage was determined iodometrically. Cleavage usually proceeded very rapidly at first, but it slowed down considerably toward the end. The major product of the cleavage was p-cyclohexylphenol. p-Isopropylphenol was also isolated in small amounts. Data from some of the experiments are presented in Table 3.

The p-cyclohexylphenol was obtained in the form of white acicular crystals; m. p. 128-129° (from benzene); literature value [1], 128°. The p-isopropylphenol was also obtained as white needles with an m. p. of 60°; literature value [2], 61°. The p-cyclohexylacetophenone was a liquid with an agreeable odor; b. p. 137-141° at 6 mm; d_4^{20} 1.0509; n_D^{20} 1.5200; molecular weight, found 201.4; calculated for $C_{14}H_{18}O$, 202.1. The 2,4dinitrophenylhydrazone of this p-cyclohexlacetophenone melted at 183°; literature data [3], b.p. 150-160° at 10 mm.

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INVESTIGATION OF THE REARRANGEMENT
OF HYDRAZO COMPOUNDS UNDER THE INFLUENCE
OF UN-IONIZED ACIDS

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This paper presents a brief report of the results of our experiments on the rearrangement of hydrazobenzene (I), 2, 2'-dimethylhydrazobenzene (II), and 2, 2'-dimethoxyhydrazobenzene (III) under the influence of dry HCl or HBr in ether, benzene–toluene mixture (b-t-m), and in the absence of a solvent (see Table 1). The method used in this investigation consisted of the following: a solution of HCl or HBr (3 moles) was added dropwise to the hydrazo compound (0.01 mole), which was completely dissolved in the minimum amount of ether or benzene–toluene mixture (2 : 1 ratio). The first 2 moles of acid were added over a period of 25-30 minutes; in certain experiments (Experiments 3 and 7), the solution of hydrazo compound was added at the same rate to the solution of acid (4 moles).

TABLE 1

Expt. No.	Charged			Temp., °C	Obtained, %						Total products, %
	hydrazo compound	acid	solvent		benzidines	diphenylines	o,o-di-amines	o-semidines	anilines	azo compounds	
1	I	HCl	Ether	−10	53.4	24.1	7.2	7.0	0.4	0.4	92.5
2	I	HCl	b-t-m	−10	29.8	26.2	10.0	17.0	4.7	4.9	92.6
3	I	HCl	b-t-m	−10	36.4	29.6	12.8	12.5	0.4	0.5	92.2
4	I	HCl	—	−10−15	21.7	20.2	17.6	29.0	1.5	1.7	91.7
5	I	HBr	Ether	−10	33.6	30.6	7.5	16.0	1.5	1.6	91.0
6	I	HBr	b-t-m	−10	25.2	25.1	3.4	13.0	13.4	13.4	93.1
7	I	HBr	b-t-m	−10	32.3	32.9	8.2	15.2	1.8	2.1	92.5
8	I	HBr	—	−10−15	17.7	18.4	10.5	25.5	11.5	1.3	84.9
9	II	HCl	Ether	−10	44.7	25.0	—	1.5	10.5	11.5	93.2
10	II	HCl	—	−10−15	22.6	23.9	—	20.1	11.7	11.5	89.8
11	II	HBr	Ether	−10	41.1	30.4	—	9.5	6.8	6.0	93.8
12	II	HBr	b-t-m	−10	36.0	29.5	—	10.2	9.5	9.2	94.4
13	II	HBr	—	−10−15	14.5	16.3	—	23.0	21.0	7.0	81.8
14	III	HBr	Ether	−10	14.0	18.2	—	18.5	20.0	18.1	88.8
15	III	HBr	b-t-m	−10	17.3	17.7	—	10.5	19.4	20.0	85.4

In the experiments without a solvent, a weak stream of HCl or HBr was passed over the surface of the finely powdered hydrazo compound while the apparatus, which was in an ice-salt mixture, was shaken slightly. Aqueous solutions of the products of the rearrangements were almost colorless.

TABLE 2

Expt. No.	Hydrazo compound, moles		Acid, moles		Solvent	Time		Residualhydrazo compound, %
1	0005	I	0,005	HCl	Ether	30	min	59
2	000125	I	0,00025	HCl	Ether	100	hr.	84
3	0005	I	0,005	HBr	Ether	2	sec	Traces
4	000125	I	0,00025	HBr	Ether	2	sec.	31
5	0005	I	0,005	HCl	EtOH	16	hr.	68
6	0,0005	I	0,005	HBr	EtOH	14	hr.	68
7	0,0005	II	0,005	HCl	Ether	2	sec	60
8	0,0005	II	0,005	HCl	EtOH	4	hr	57
9	0,0005	II	0,005	HBr	EtOH	2	hr	65
10	0,0005	IV	0,C01	HBr	Ether	425	hr	99
11	0,0005	IV	0,005	HCl	b-t-m	200	hr	64
12	0,0005	IV	0,001	HBr	b-t-m	5	sec	46

Analysis of the reaction mixtures was considerably simplified by first separating the o-semidines; this was accomplished by repeatedly treating the aqueous solutions with ether, thereby completely extracting the weakly basic o-semidines, which were again converted to the salt by agitating the ether solutions with 10-15% HCl. The azo compounds remained in the organic solvent. The o-semidines were determined quantitatively by titration with nitrite. The o-semidines formed by the rearrangement of (II) and (III) have not previously been described; 2, 3'-dimethyl-2'-aminodiphenylamine crystallized as massive tablets (from petroleum ether), m. p. 91°; 2, 3'-dimethoxy-2'-benzoylaminodiphenylamine crystallized as tetragonal prisms (from alcohol), m: p. 156-157°.

The formation of 4-bromo-2'-aminodiphenylamine (m. p. 127-128°) and 4-bromo-2, 3'-dimethyl-2'-aminodiphenylamine (proposed structure, m. p. 105-107°) during the rearrangement of crystalline (I) and (II) with HBr is interesting; when the experiments were carried out in solvents, the amount of brominated semidines was insignificant. In addition, large amounts of aniline (Experiment 8) and o-toluidine (Experiment 13) were obtained. The brominated o-semidines were products of secondary reactions; the hydrobromide of the hydrazo compound was formed, and this was reduced by the hydrogen bromide with simultaneous bromination of the o-semidine. As a matter of fact, we satisfied ourselves that when highly dilute solutions of o-aminodiphenylamine hydrobromide in ether and of bromine (in benzene) are mixed, 4-bromo-2'-aminodiphenylamine is immediately formed in a yield of 90% of theoretical.

After removal of the o-semidines, the remaining substances were easily determined. Benzidine was reprecipitated twice as the sulfate; the aniline was redistilled with steam; diphenyline and o, o'-diaminobiphenyl were converted to the benzoyl derivatives and completely separated and purified by means of alcohol and ether. o-Toluidine and o-dianisidine were salted out of solutions made strongly acid with HCl and were purified (the dianisidine was salted out of solution in 20% H_2SO_4). The filtrates were used for the determination of o-toluidine, o-anisidine, and diphenylines by the method described above. The latter compounds have not previously been characterized; 3, 3'-dimethyl-2, 4'-dibenzcyldiamidobiphenyl crystallized in tetragonal prisms (from acetone, m. p. 245-246°; 3, 3'-dimethoxy-2, 4'-dibenzoyldiamidobiphenyl crystallized as drusy prisms (from xylene), m. p. 269°; we may also mention that 3, 3'-dimethoxy-4, 4'-dibenzoyldiamidobiphenyl melts at 252°.

It is evident that rearrangement in un-ionized acids is characterized by a sharp reduction in the amounts of benzidine and analogs with a similarly sharp increase in the yields of isomers. Anilines and azo compounds—products of an intermolecular oxidation—reduction reaction—are usually formed in insignificant amounts in the presence of excess acid (Experiments 3 and 7).

Rates of rearrangement of hydrazo compounds. The rearrangement rates in the presence of un-ionized acids frequently so sharply differ among themselves and so far exceed the rates in aqueous alcohol solutions that their comparison is very difficult. Nevertheless, for orientation purposes it is necessary to present some figures relating to hydrazobenzene (I), 2, 2'-dimethylhydrazobenzene (II), and 2, 2'-dichlorohydrazobenzene (IV). All experiments were carried out at 0-1° C; 95% alcohol was used.

It is especially interesting that in the un-ionized state, HBr behaves as a much stronger acid than HCl; the rearrangement rate in the presence of HBr exceeds that in the presence of HCl by a factor of hundreds of thousands, and only results obtained in the same solvent, ether (Experiments 2 and 4) or benzene-toluene solutions (Experiments 11 and 12), can be compared, since the rate was immeasurably greater in benzene—toluene solution than in ether solution (see Experiments 10 and 11 or 12). It should also be noted that the weaker base (II) rearranged almost a thousand times more rapidly in an ether solution of HCl than did base (I)(see Experiments 1 and 7). Similar relationships were encountered in other experiments (see Table 3).

The experiments were carried out as follows: 25 ml of acid was mixed with 75 ml of the hydrazo compound, the reaction was stopped by adding a solution of NaOH in alcohol, and the hydrazo compound was oxidized

with an excess of mercuric oxide. The azo compounds in the benzene—toluene and the ether solutions were separated by treatment with dilute and, finally, concentrated HCl, and the azobenzene and o-azotoluene were steam distilled and quantitatively determined colorimetrically and also by a gravimetric method (in the case of IV).

TABLE 3

Expt. No.	Hydrazo compound (0.001 mole in 100 ml of solution)	Unrearranged hydrazo compound from reaction with HCl in ether, % of that charged			Yield of hydrazo salt, %	Chloroanilines with which the hydrazo compounds compare in basicity
		0.02 mole HCl, 10 sec	0.001 mole HCl			
			10 sec	20 min.		
1	Hydrazobenzene	–	–	62	92	Bet. 2,4- and 2,5-
2	2-Chlorohydrazobenzene	–	–	83	66	2,3,4,5,6-
3	3-Chlorohydrazobenzene	–	–	89	88	Bet. 2,3,5,6- and 2,3,4,5,6-
4	4-Chlorohydrazobenzene	–	94	Traces	10	2,3,5,6-
5	3,3'-Dichlorohydrazobenzene	–		100	54 (HBr)	2,3,4,5,6-
6	2-Methylhydrazobenzene	94	31	–	13	2,4,6-
7	3-Methylhydrazobenzene	–	78	–	90	Bet. 2,5- and 2,4,5-
8	2,2'-Dimethylhydrazobenzene	75		–	None	2,6-
9	3,3'-Dimethylhydrazobenzene	87	50	–	90	Bet. 2,5- and 2,4,5-
10	4,4'-Dimethylhydrazobenzene	Traces	–	–	None	2,4-
11	2,2'-Dimethylhydrazobenzene	–	Traces	–	None	2,4,5-
12	3,3'-Dimethoxyhydrazobenzene	98	44	–	44	2,4,6-

Salts of hydrazo compounds [1]. Ether solutions of hydrogen halides can be considered as equilibrium systems* :

$$[(C_2H_5)_2 \overset{+}{O}H] \bar{X} \rightleftarrows (C_2H_5)_2O \ldots HX. \tag{1}$$

Since the HX become weaker acids as the result of the intermolecular interaction, it is easy to obtain salts of hydrazo compounds in ether (see Table 3). As may be seen, salts of hydrazo compounds having substituents in the 3- or 3, 3'-positions with respect to the hydrazo group are relatively stable, but stable 2, 2'- and 4, 4'-substituted salts are not formed. It is possible to show that a slat is formed in the case of 4-chlorohydrazobenzene; when an ether solution of HCl (1 mole) is rapidly introduced, a voluminous precipitate of the salt is immediately formed, and if the mixture is slowly made alkaline and the hydrazo compound oxidized, a 93-94% yield of 4-chloroazobenzene is obtained. In experiments carried out in the same manner with 4, 4'-dichloro- and 2, 2'-dimethylhydrazobenzene, the yields of azo compounds were 55-60% and 60-65%, respectively.

Basicity of hydrazo compounds. Many hydrazo compounds can be compared to the chloroanilines with respect to basicity. If one takes, for example, equimolar amounts of hydrazobenzene, 2, 4-dichlorcaniline, and HCl or HBr in ether, then regardless of the order of mixing these reagents, an equilibrium is immediately established; about 14% of the hydrazobenzene separates as the salt, and 85% remains in solution. If 2, 5-dichloroaniline is substituted for the 2, 4-dichloroaniline, 69% of the hydrazobenzene forms the salt, and about 30% remains in solution; with 2, 4, 5-trichloroaniline, 86% of the hydrazo compound forms the salt, and 11% remains in solution; and, finally, with 2, 6-dichloroaniline, 94% forms the salt and 3-4% remains in solution. Hence, it may be concluded that hydrazobenzene is a somewhat stronger base than 2, 5-dichloroaniline. The situation is more complex in the cases of unstable salts of hydrazo compounds; if one takes, for example, 2, 2-dimethylhydrazobenzene, 2, 5-dichloroaniline, and HCl, the acid is completely combined with the dichloroaniline; the situation is almost the same with 2, 4, 5-trichloroaniline, but rearrangement proceeds intensively in the presence of 2, 6-dichloroaniline; hence, it may be concluded that 2, 2'-hydrazobenzene is about as basic as 2, 6-dichloroaniline. The less basic hydrazo compounds (2-chloro- and 3, 3'-dichlorohydrazobenzene) are comparable to pentachloroaniline;

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* Since these solutions are electrically conducting [2], they contain diethyloxonium ions; however, considering the enormous difference in the rates of rearrangement in ether solutions of HCl and HBr, it is evident that participation of these ions in the rearrangement need not be considered.

HBr should be used in these cases, since the hydrochlorides of these bases are highly dissociated in ether. 2, 2'-Dichlorohydrazobenzene is a much weaker base than pentachloroaniline. Unfortunately, at present we cannot numerically express the basicities of these chloroanilines. According to the literature [3], the pK's of o-, m-, and p-chloroanilines and 2, 4-dichloroaniline are, respectively, 11.32, 10.46, 9.97, and 11.86.

   The mechanism of the rearrangement. Does the hydrazo compound rearrange in the form of a mono- or a diprotonated cation? This is a basic question which has been the subject of numerous investigations [4]. We have shown for a number of cases [5] that, in the absence of any considerable excess of acid, salts of hydrazo compounds undergo an oxidation—reduction reaction almost exclusively:

$$2(RNH \cdot \overset{+}{N}H_2R)\,\overline{C}l \rightarrow RN = NR + 2R\overset{+}{N}H_3\overline{C}l \tag{2}$$
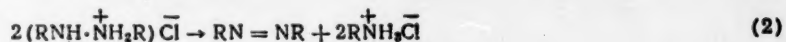
Consequently, the participation of a second molecule of acid in the rearrangement is inevitable. It was decided to determine to what extent diacid salts are really formed in the mixed aliphatic aromatic hydrazine series. N-methyl-N'-phenylhydrazine was synthesized by Knorr's method [6] (b. p. 80-82° at 2 mm), and we found that with HCl and HBr in ether and in benzene (b-t-m), the monoacid salt crystallized out quantitatively (from elemental analysis). Special experiments showed that significant amounts of the diacid salt do not form: to a solution of hydrazine (1 mole) in a small amount of solvent was added HCl or HBr (4-7 moles) in an amount such that 0.15-0.30 mole of acid remained in the solution after the reagents had reacted, and after 1 hour, from $^1/_3$ to $^1/_2$ of the transparent solution was separated; titration of both parts showed that in all cases 1 mole of acid combined with the hydrazine. For comparison, it may be mentioned that 2, 4-dinitroaniline (pK = 18.40) in dilute benzene solution is essentially combined with the HBr (HBr concentration = 0.10 mole). As may be seen, salts of mixed aliphatic aromatic hydrazines are very weak bases. It is also clear that in a number of cases, it is difficult to relate the enormous rearrangement rates of the much weaker bases—salts of hydrazo compounds—to the insignificant traces of diprotonated hydrazo compounds which may be present in the reaction mixtures. It seems more probable to us that the mechanism is an intermolecular interaction (hydrogen bonding?) of the polar molecules—the salt of the hydrazo compound and the acid—between which equilibrium is established at ionic reaction rates:

$$(RNH \cdot \overset{+}{N}H_2R)\,\overline{X} + HX \rightleftharpoons (RNH \cdot \overset{+}{N}H_2R)\,\overline{X} \ldots HX \rightarrow \begin{matrix} \text{Rearrangement} \\ \text{products} \end{matrix} \tag{3}$$
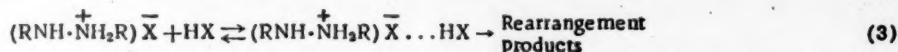
   If the rate of salt formation is determined by the basicity of the given hydrazo compound, then the rate of the irreversible formation of the rearrangement product is closely connected with the stability of the salt under the reaction conditions, only indirectly depending on the basicity of the hydrazo compound.

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THE INFRARED SPECTRA AND STRUCTURE
OF LITHIUM ACETYLIDES

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In previously published work [1], we have studied the infrared spectra and dipole moments of aliphatic organolithium compounds. It was established that R—Li compounds form complexes by means of a "lithium bond", both in solution and in the crystalline state. The C—Li bond in these compounds is covalent but polar ($\mu = 1.1$–$1.2D$). The study of the structure and nature of the C—Li bonds in organolithium compounds of the ethylene and acetylene series is of great interest. The literature contains almost no information on this question in spite of the widespread use of these compounds in synthesis.

In this connection, new data obtained from a study of the structure of certain organolithium compounds of the acetylene series would appear to be of interest. That acetylene itself and its derivatives are capable of forming complexes by themselves and with certain solvents, both through hydrogen bonding and by means of the π electrons of the $\equiv C$ group [2] lends interest to the study of the lithium compounds. It is natural to assume that replacement of a hydrogen atom by a lithium atom in acetylene and its derivatives could only increase the ability of these compounds to form complexes of the following types in which electrons of the C—Li bonds and π electrons of the $C \equiv C$ groups take part:

$$R - C \equiv C - Li \qquad \text{and} \qquad R - C \equiv C - Li...X \quad (X - O\langle \; ; N\langle).$$
$$Li - C \equiv C - R$$
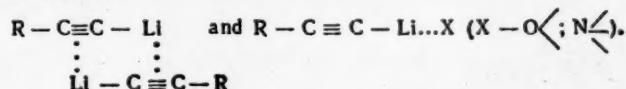
With the aim of clarifying the structure of this class of compounds, we have investigated the spectra of lithium acetylide, lithium methylacetylide, lithium tert-butylacetylide, and lithium phenylacetylide. Moreover, for purposes of comparison, the spectra of potassium and sodium acetylides and phenylacetylides, of acetylene, methylacetylene, ethylacetylene, and tert-butylacetylene in the vapor state, and of liquid phenylacetylene were obtained using the same apparatus. Spectra were obtained for all of the acetylides in the solid state and in vaseline and fluorinated oils, and, in addition, the spectrum of lithium tert-butylacetylide in hexane solution was measured.

The lithium acetylides were prepared by metallation of acetylene and alkylacetylenes with organolithium compounds; the reactions were carried out at a temperature of $0°$ to $-50°$ in hexane, ether, benzene, or octane. The yields were almost quantitative. Compounds of the general formula RLi, where R is CH_3, C_2H_5, C_4H_9, C_5H_{11}, C_6H_5, or $CH_3C_6H_5$, were used as the metallating agents.

The results are presented in Figs. 1 and 2 and in Table 1.

Let us now consider in some detail the spectra of lithium, sodium, and potassium acetylides and of acetylene. The spectra of acetylene and sodium acetylide have no absorption bands in the 700 to 1300-cm^{-1} region, while the spectrum of potassium acetylide exhibits several relatively weak, diffuse bands. In this same region, the spectrum of lithium acetylide has a whole series of sharp, intense bands (Fig. 1). The most intense bands in the spectra of all of the lithium acetylides prepared using the different organolithium compounds and the different

TABLE 1

Compound	≡C—Li		C≡C	≡C—H
	in complex	free		
Lithium acetylide (cr.)	1060 av, 1082 s	—	1990 w	3245 av
Sodium acetylide (cr.)	— —	—	—	3216 s
Potassium acetylide (cr.)	—	—	—	3224 av
Lithium methylacetylide (cr.)	935 vs 1083 s	—	2225 w	—
Lithium ethylacetylide (cr.)	928 av 1081 s	—	2217 av	—
Lithium tert-butylacetylide (cr.)	1080 s	—	2200 s	—
Same (conc. solution in hexane)	1083 s	—	2205 av	—
Lithium phenylacetylide (cr.)	1052 s	1196 av	2213 s	—
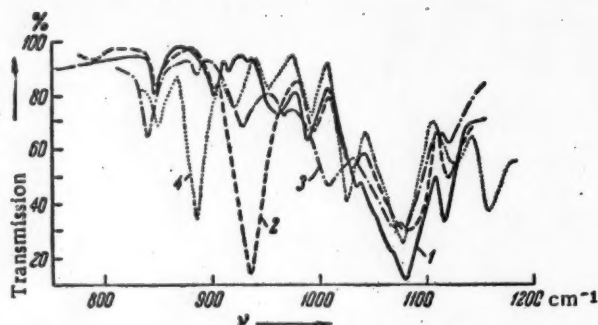
Fig. 1. I. r. spectra of crystalline lithium acetylides. NaCl prism. 1—lithium acetylide; 2—lithium methyl-acetylide; 3—lithium ethylacetylide; 4—lithium tert-butylacetylide.

solvents were located at about 1060 and 1090 cm^{-1} The relative intensities of these two bands varied with the type of solvent. Since these bands appear only in the spectra of lithium acetylide, there is good reason to assign them to the C—Li group. However, an approximate calculation of the vibrational frequency of the C—Li bond, assuming only a small change in the force constants for aliphatic organolithium compounds as compared to those of acetylides, gives for the C—Li bond a frequency of about 1200 cm^{-1}. Hence, the bands at about 1060 and 1090 cm^{-1} in the spectra of lithium acetylide apparently cannot be assigned to the free C—Li group. These data, in conjunction with the nonvolatility, the insolubility, and other properties of lithium acetylide, leads to the conclusion that the molecules of this compound form stable complexes, and the bands at about 1060 and 1090 cm^{-1} are apparently assignable to C—Li groups participating in the formation of complexes between molecules of lithium acetylide. When the lithium acetylide was prepared in ether or liquid ammonia, it was possible to separate lithium acetylide etherate and ammoniate. In addition to the bands observed previously, ether bands also appeared in the spectrum of the etherate. In the case of the ammoniate, the lithium acetylide bands were no longer apparent, but an intense band appeared at about 1128 cm^{-1}; this band disappeared when the substance was slightly heated under vacuum, evidently owing to decomposition of the ammoniate complex. Therefore, the band at about 1128 cm^{-1} can apparently be assigned to the C—Li bond in this complex. It is interesting that according to both the literature [3] and our own data, the monomeric lithium acetylide resulting from the decomposition of the ammoniate is unstable and spontaneously transforms to lithium carbide. It is evident that even during preparation, lithium monoacetylide begins to form complexes either with itself (in hexane medium) or with the solvent (in liquid ammonia), and the monomeric acetylide resulting from the decomposition of these complexes immediately decomposes to lithium carbide and acetylene. The absence of the lithium carbide band in this region can be explained by a change in the nature of the bond in the carbide and the approach toward an ionic or metallic bond. In order to confirm that we were actually dealing with acetylides, in each case a spectrum was measured in the region from 1900 to 2300 cm^{-1} where bands characteristic of C≡C vibrations should appear. The spectrum of solid lithium monoacetylide had a low-intensity band at about 1990 cm^{-1} which may be assigned to C≡C vibrations.

Another region of the spectrum useful for determining the structure of acetylides is the region in which valence vibrations of $\equiv$C$-$H appear. The frequency of this vibration was found to be 3315 cm^{-1} for gaseous acetylene, 3224 cm^{-1} for crystalline sodium and potassium acetylides, and 3245 cm^{-1} for lithium acetylide. Such a considerable decrease in the frequency of vibration of the C$-$H bond in acetylides as compared to the vibrational frequency of this same bond in acetylene cannot be explained merely by the difference in the states of the compounds. Evidently, this decrease in frequency is due to participation of the remaining hydrogen in the monoacetylide in an intermolecular interaction, a phenomenon which also occurs in acetylene itself in various solvents [2].
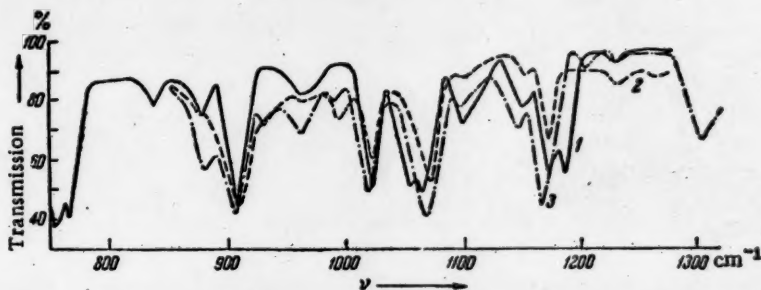
Fig. 2. I. r. spectra of lithium, sodium, and potassium phenylacetylides. NaCl prism. 1—lithium phenylacetylide; 2—sodium phenylacetylide; 3—potassium phenylacetylide.

Bands in the 800-1200-cm^{-1} region, close to those in the spectrum of lithium acetylide (Fig. 1 and Table 1), were present in the spectra of lithium methylacetylide, ethylacetylide, and tert-butylacetylide and were not present in the spectra of methylacetylene, ethylacetylene, and tert-butylacetylide vapors. As in the spectrum of lithium monoacetylide, the most intense of these bands were again the bands at about 1060 and 1080 cm^{-1}, which are apparently connected with the formation of the same types of complexes in the crystals of all acetylides. But apart from these bands, a new, very intense band was present in the spectra of lithium methylacetylide and ethylacetylide at about 935 cm^{-1} and 928 cm^{-1}, respectively; this band was not present in the spectra of the compounds considered above, and was apparently connected with some other type of complex.

In the region of C$\equiv$C vibrations, two bands at about 2050-2070 cm^{-1} and 2220 cm^{-1} were present in the spectra of lithium methylacetylide, ethylacetylide, and tert-butylacetylide. The band in the 2220 cm^{-1} region is in good agreement with the data on the vibrational frequency of the C$\equiv$C bond in disubstituted acetylenes [5].

A number of authors [4, 5] have noted the appearance in the spectra of monosubstituted acetylenes of a single C$\equiv$C valence vibration band, while two and more bands have been observed in this region for disubstituted acetylenes; these bands correspond to an overtone or combination frequency, and their intensity is increased by resonance. Therefore, in our case, the band at about 2070 cm^{-1} is evidently an overtone of the very intense band at 1080 cm^{-1}, strengthened and shifted by Fermi resonance between the vibrational frequency of the C$\equiv$C bond and the first overtone, 2 x 1080. The vibrational frequencies for C$-$H bonds in methyl and ethyl radicals appeared in the region of 2840-2960 cm^{-1}, i. e., in the region where they should appear according to the literature [5].

We also investigated the spectra of lithium, sodium, and potassium phenylacetylides and that of phenylacetylene itself (liquid) (Fig. 2). A comparison of these spectra shows that in the 800-1300-cm^{-1} region, the spectrum of phenylacetylene is well reproduced in the spectra of all of the acetylides; however, in addition to the phenylacetylene bands in this region, new, intense bands were present in the spectrum of lithium phenylacetylide at about 1052 and 1196 cm^{-1}. It should be noted that the intensity of these bands depends on the medium in which the lithium phenylacetylide is prepared. Thus, in the spectrum of the lithium phenylacetylide prepared in benzene, both bands were rather intense, while when the lithium phenylacetylide was prepared in hexane, the intensity of the band at about 1052 cm^{-1} decreased sharply and that of the band at about 1196 cm^{-1} increased somewhat.

A comparison of these values for lithium phenylacetylide with the results of the calculation mentioned above suggests that the frequency at about 1200 cm^{-1} can be assigned to the $\equiv$ C—Li bond in free or weakly bonded molecules of lithium phenylacetylide and the frequency at about 1052 cm^{-1} to this bond in the complex. In the region of C $\equiv$ C valence vibrations, three intense bands at about 1964, 2057, and 2213 cm^{-1} were found in the spectrum of lithium phenylacetylide. We assign the last band to the C $\equiv$ C valence vibration, while, as before, the remaining two bands can be assigned to overtones or combination frequencies.

Thus, the present work has shown that the molecules of lithium acetylides in crystals form stable complexes, both among themselves and with other compounds (ammonia). The bands at about 1060 and 1080 cm^{-1} can be assigned to valence vibrations of the $\equiv$ C—Li group in complexes. The frequency of the valence vibration of the free $\equiv$C—Li group is apparently about 1200 cm^{-1}, as observed in the case of lithium phenylacetylide. These data confirm our previous assumption [6] that lithium acetylides have a greater tendency toward the formation of complexes than does acetylene itself. This may be explained by the increased polarity of the $\equiv$ C—Li bond (as compared to the $\equiv$ C—H bond) and also by the greater likelihood of the valence electron of the lithium atom of being promoted to a p orbital.

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INVESTIGATIONS OF TRITERPENES.
MYRICADIOL FROM THE BARK OF MYRICA GALE L.

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(Presented by Academician B. A. Arbuzov, June 22, 1959)

We have isolated a new triterpene, $C_{30}H_{50}O_2$, m. p. 273-274°, from the bark of Myrica gale L., and we have selected the name myricadiol for this compound. That this is a single substance was proved by saponification of the diacetate to the original compound with the same melting point. Oxidation of myricadiol with chromium trioxide in pyridine gave the dioxo compound $C_{30}H_{46}O_2$, which formed a disemicarbazone. The spectrum of this compound, which we have named myriconal, had two absorption bands, one at 1709 cm^{-1} (cyclohexanone) and one at 1726 cm^{-1} (aldehyde). Consequently, myricadiol is a primary-secondary diol.

Wolff-Kishner reduction of myricadiol gave the hydrocarbon $C_{30}H_{50}$, which was shown to be taraxerene (I, R = H; R' = CH$_3$).
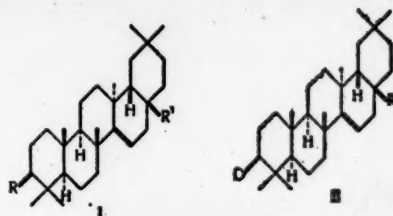
In order to identify this compound, taraxerene was prepared from taraxerone. Taraxerone (II, R = CH$_3$) and taraxerol (I, R = OH; R' = CH$_3$) have been found in the bark of various species of alder [1]. We isolated taraxerone from the bark of Alnus incana (L.) Moench. It was identified by reduction to taraxerol and comparison of the absorption spectrum of the latter in the 1800-800-cm^{-1} region with the spectrum reported in the literature for taraxerol [2]. The taraxerene prepared by Wolff-Kishner reduction of taraxerone was found to be identical with that prepared from myricadiol. That these compounds were identical was shown by mixed melting point and by a comparison of the absorption spectrum in the region from 1800 to 800 cm^{-1}. It is well known [3] that saturation of a solution of taraxerene at room temperature with hydrogen chloride over a period of several minutes converts the taraxerene to olean-12-ene (III, R = H; R' = CH$_3$).
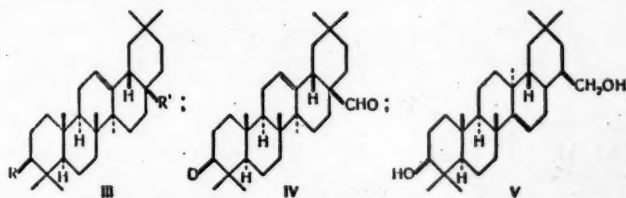
In our experiment, which was carried out under these conditions, the taraxerene prepared from myricadiol was completely isomerized to olean-12-ene.

It has thus been shown that myricadiol is a taraxerendiol. Acid-catalyzed isomerization should convert it to the corresponding olean-12-endiol. Actually, the action of hydrogen chloride on a chloroform solution of myricadiol did yield the isomeric diol. The diacetate of this same oleandiol was prepared by heating an acetic acid solution of myricadiol in the presence of hydrochloric acid. The oleanendiol formed by the acid-catalyzed rearrangement of myricadiol was identified as erythrodiol (III, R = OH; R'= CH$_2$OH) by determination of the melting point and $[\alpha]_D$ of the diol and diacetate and the melting point of the diformate. Acid-catalyzed isomerization of myriconal (II, R = CHO) should lead to the formation of oleanonic aldehyde (IV); this keto aldehyde is presently not known, and only its mono- and dioxime have been prepared [4]. The keto aldehyde formed in our experiment on the isomerization of myriconal did not have a definite melting point; the melting point of the dioxime, was in agreement with that reported in the literature for the dioxime of oleanonic aldehyde.

The facts cited above demonstrate that the structure of myricadiol is that of 14-taraxerene-3β, 28-diol (V).

EXPERIMENTAL

The benzene extract of 5 kg of dry bark of Myrica gale L. was evaporated, and the residue was dissolved in a large amount of boiling acetone. The solution was allowed to stand, and crystals of myricadiol, m. p. 273-274° (1.5 g), precipitated; evaporation of part of the acetone yielded another 24 g of almost pure material; after reprecipitation from dioxane, this substance melted at 273-274°. When a saturated solution of myricadiol in dioxane was cooled, a transparent gel was formed, and, after several days, sometimes weeks, clusters of needles and solvent began to separate from the solution.

Found %: C 81.42; 81.39; H 11.72; 11.71
C$_{30}$H$_{50}$O$_2$. Calculated %: C 81.39; H 11.38.

The diacetate of myricadiol melted at 256.5° $[\alpha]_D \pm 1°$ (conc. 0.8), after recrystallization from alcohol.

Found %: C 77.72; 77.66; H 10.33; 10.86
C$_{34}$H$_{54}$O$_4$. Calculated %: C 77.52; H 10.33.

Saponification of the diacetate by a methanol solution of potassium hydroxide gave myricadiol with an m. p. of 273-274°.

Myriconal. 1.5 g of myricadiol was dissolved in pyridine, a solution of 1.5 g of chromium trioxide in pyridine was added, and the mixture was allowed to stand overnight. Myriconal crystallized from alcohol-benzene mixture as plates with an m. p. of 256-257°.

Found %: C 82.26; H 10.58
C$_{30}$H$_{48}$O$_2$. Calculated %: C 82.13; H 10.57

The melting point of the disemicarbazone was 298°, and that of the bis-2, 4-dinitrophenylhydrazone was 247°. Analysis of the disemicarbazone gave:

Found %: N 15.33
C$_{32}$H$_{56}$O$_2$N$_6$. Calculated %: N 15.09.

Taraxerene. a) A solution of 0.7 g of myriconal, 30 ml of diethylene glycol, and 1 ml of hydrazine hydrate (100%) was refluxed for an hour. A solution of 0.7 g of potassium hydroxide in 10 ml of diethylene glycol was added, the water and hydrazine hydrate were distilled, and the reaction was further carried out at 230-240° for 9 hours. When the reaction mixture was cooled, crystals with an m. p. of 239-240° (0.65 g) precipitated; after recrystallization from alcohol-benzene mixture, the crystals melted at 241-242°, $[\alpha]_D \pm 2°$ (conc. 0.32). Literature data: m. p. 242-244°; $[\alpha]_D +3°$ [3].

Found %: C 87.80; 87.89; H 12.05; 11.86
C$_{30}$H$_{50}$. Calculated %: C 87.73; H 12.27.

b) Taraxerone with an m. p. of 240-242° (literature value, 241-243° [4a]) was extracted from the bark of the grey alder. Reduction with sodium in isobutyl alcohol converted this compound to taraxerol with an m. p. of 278-280° (literature value, 279-281° [4b]). 200 mg of taraxerone and 1.5 g of anhydrous hydrazine hydrate in 10 ml of diethylene glycol were heated at 200° for 8.5 hours, 0.2 g of potassium hydroxide was added, and the reaction was carried out for an additional 8 hours at 220°. The precipitated crystals had an m. p. of 240°, which increased to 242° when the substance was recrystallized from benzene-alcohol mixture.

A mixture of the hydrocarbons prepared in Experiments a and b melted at 242 deg. The spectra of these substances in the 1800-800-cm^{-1} region were identical.

Olean-12-ene. Hydrogen chloride was passed for 3 minutes into a solution of 80 mg of taraxerene (from Experiment a) in 25 ml of chloroform; the solution was washed with a solution of base and evaporated. After recrystallization from methanol-chloroform mixture, the olean-12-ene melted at 161.5-162.5°, $[a]_D$+ 101° (conc. 0.32). Literature data: m. p. 160-161°, $[a]_D$+96° [3].

Erythrodiol. a) 300 mg of myricadiol in 30 ml of acetic acid containing 1.5 ml of hydrochloric acid was heated for 10 minutes at 90°. Erythrodiol acetate separated; it was recrystallized from alcohol, after which it melted at 184.5-185.5°, $[a]_D$+60° (conc. 0.8). Literature data: 184-185°, $[a]_D$+59° [5].

$$C_{34}H_{54}O_4. \quad \text{Found \%: C 77.52; 77.36; H 10.56; 10.54} \\ \text{Calculated \%: C 77.27; \qquad H 10.62.}$$

The diacetate of erythrodiol was saponified by refluxing in a methanol solution of potassium hydroxide. The erythrodiol melted at 231.5-232.5°, $[a]$+ 83° (conc. 1.2). Literature data: m. p. 235-237°, $[a]_D$+ 76°, +80° [5].

$$C_{30}H_{50}O_2. \quad \text{Found \%: C 81.49; 81.42; H 11.60; 11.66} \\ \text{Calculated \%: C 81.39; \qquad H 11.38.}$$

b) Hydrogen chloride was passed for 2 hours into a solution of 500 mg of myricadiol in 100 ml of chloroform. The substance which separated had an m. p. of 228-230°. A mixture of this material with erythrodiol prepared in Experiment a melted at 231-232°. The diformate, m. p. 195-197°, was prepared. Literature data: m. p. 195° [4a].

Oleanonic aldehyde. Isomerization of myriconal under the conditions of the preceding experiment gave a substance which did not have a definite melting point: the dioxime melted at 264°. Literature data: m. p. 263° [4a]. The specific rotations were determined in chloroform solutions. The spectra were measured with a suspension of the material in vaseline oil.

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DEHYDROGENATION OF n-NONANE
OVER CHROMIA-ALUMINA CATALYST

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In some of our previously published work [1], we studied the conversion of straight-chain hydrocarbons, including n-nonane, over potassium-promoted chromia-alumina catalyst. Catalyzates containing up to 13.5% olefins were obtained by passing these hydrocarbons over the catalyst at 500° and a space rate of 0.5 hours^{-1}. However, up to 39% aromatic hydrocarbons were present in the catalyzates. We further found that by using chromia-alumina catalysts without alkaline promoters, the ratio of the yield of unsaturated hydrocarbons to that of aromatic hydrocarbons could be increased significantly. For example, when the hydrocarbon was passed at 500° and a space rate of 0.5 hours^{-1} over a chromia-alumina catalyst having the composition 94.2 mole % Al_2O_3 and 5.8 mole % Cr_2O_3, n-hexane yielded a catalyzate containing 23% unsaturated hydrocarbons and 16% aromatic hydrocarbons. Under these same conditions but with a potassium-promoted chromia-alumina catalyst, the catalyzate from n-hexane contained 13.7% olefins and 43% aromatic hydrocarbons. Under different conditions—at 475° and a space rate of 2.1 hours^{-1}—and in the presence of an unpromoted chromia-alumina catalyst, we obtained a catalyzate which contained practically no benzene, while the hexene content was 12% [2].

TABLE 1

Properties and Compositions of Catalyzates Obtained by Dehydrogenation of n-Nonane over Chromia-Alumina Catalyst

Amt. of n-nonane fed, ml	Temp., °C	Space rate, hr^{-1}	Catalyzate yield, %	Amt. of gas formed, ml (STP)	n_D^{20}	Content in catalyzate, %	
						of unsaturates	of aromatics
100	400	2,1	98,6	2000	1,4085	7,8	<1
200			98,7	3800	1,4085	7,6	<1
100	450	2,1	95,5	9100	1,4175	13,1	8,0
200			96,0	16350	1,4165	12,4	8,5
100	475	2,1	93,0	13100	1,4245	15,1	16,4
200			94,0	22700	1,4225	13,9	14,5
100	427	4,2	98,6	2800	1,4100	9,4	1,8
200			98,3	5100	1,4095	8,8	<1
700			98,7	12750	1,4095	7,9	<1
100	475	4,2	93,0	9000	1,4190	14,1	11,5
200			93,5	16000	1,4170	13,7	10,0

It seemed to be of interest to investigate the dehydrogenation of n-alkanes of higher molecular weight over such a catalyst, the more so since very little work in this field has been reported in the literature. Thus, only in the paper by Hoog [3], who studied the dehydrocyclization of C_6–C_9 n-alkanes, has data been reported on the

content of aromatic and unsaturated hydrocarbons in the catalyzate from n-nonane. At 465° and a space rate of 0.22 hours^{-1} over chromic oxide, these authors obtained 52% aromatic hydrocarbons and 15% unsaturated hydrocarbons.

The temperature and space-rate dependence of n-nonane dehydrogenation over unpromoted chromia-alumina catalyst was investigated in the present work [2]. The experimental method and the method used in analyzing the catalyzates have been described in a preceding communication [2]. The reaction was carried out at atmospheric pressure in a flow system. The amount of catalyst was 30 ml. 200 ml of n-nonane (b. p. 150.6°; n_D^{20} 1.4055; d_4^{20} 0.7182) was used in each experiment. The duration of an experiment was 3 hours and 10 minutes at a space rate of 2.1 hours^{-1} and 1.5 hours at a space rate of 4.2 hours^{-1}. Either the catalyzate corresponding to 200 ml of n-nonane feed or half that amount was analyzed; in addition, certain specific portions of the catalyzate, each corresponding to 10 ml of n-nonane feed, were analyzed, which permitted us to plot a curve showing the change in catalyst activity with time (Fig. 1).
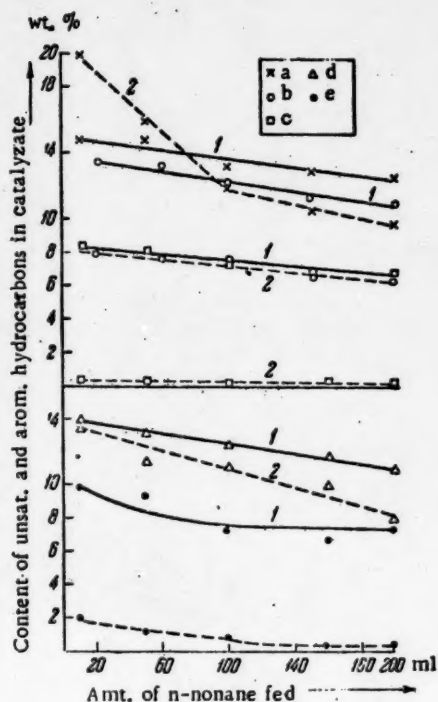
Fig. 1. Content of unsaturated (1) and aromatic (2) hydrocarbons in n-nonane catalyzates as a function of the amount of n-nonane fed. a, b, c—space rate of 2.1 hours^{-1}; a—475°, b—450°, c—400°; d, e—space rate of 4.2 hours^{-1}; d—475°, e—427°.

The gas formed during the reaction contained from 92 to 97% hydrogen, from 1.5 to 3.5% unsaturated hydrocarbons, and from 1.0 to 4.5% unsaturated hydrocarbons. The results are presented in Table 1 and Fig. 1.

As may be seen from the data presented in Table 1, an increase in the temperature from 400 to 475° at a space rate of 2.1 hours^{-1} was accompanied by an increase in the olefin content from 8% to only 14-15%; however, at the same time there was a very great increase in the aromatics content, namely, from traces to 15-16%. Thus, from the point of view of selectivity at a space rate of 2.1 hours^{-1}, the most suitable temperature for the dehydrogenation of n-nonane is 400°.

At 475°, an increase in the space rate from 2.1 hours^{-1} to 4.2 hours^{-1} had almost no effect on the olefin yield; however, at the same time the content of aromatic hydrocarbons decreased by approximately 50%— from 15-16% to 10-12%. At 427° and a space rate of 4.2 hours^{-1}, aromatic hydrocarbons, in small amounts, were formed only in the beginning of the experiment, after which their content in the catalyzates was within the limits of error of the determinations (less than 1%). The olefin content was 9% under these conditions. When 700 ml of n-nonane, instead of 200 ml, was passed over the catalyst, the olefin content decreased by only 1%. Under these conditions, the catalyst was active for the dehydrogenation of n-nonane for 11.5 hours without regeneration, during which time its activity decreased very slightly only during the first 1.5 hours of operation and then remained practically constant; the olefin content of the catalyzate was 8%, while aromatic hydrocarbons were almost completely absent.

With the aim of studying the composition of the unsaturated hydrocarbons, the catalyzate obtained in the experiment carried out at 475° and a space rate of 2.1 hours^{-1} was passed over silica gel treated with HCl and hydrogen peroxide under the conditions described by Topchiev and co-workers [4]. This procedure separated the paraffinic part of the catalyzate and a 95% concentrate of unsaturated hydrocarbons, which was then analyzed by Raman spectroscopy. This established that the olefins consisted chiefly of 4-nonene. However, it is possible that other nonenes were present, but in amounts which could not be detected by this method. Judging by the physical constants, the paraffinic part consisted of pure n-nonane, and this was confirmed by gas-liquid chromatography using an apparatus similar to that previously described by us [2]. The absence of isoalkanes with a tertiary carbon atom from the n-paraffinic part of the catalyzate was also indicated by a negative ferric chloride test [5].

Thus, the present work has shown that it is possible to carry out selective dehydrogenation of n-nonane in the presence of chromia-alumina catalyst with nonene yields of 8-9%, and without the occurrence of appreciable aromatization.

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*Original Russian pagination. See C. B. translation.

OXIDATION OF HEXAETHYLDILEAD
WITH CERTAIN ARALKYL HYDROPEROXIDES

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It is well known that hexaethyldilead is readily oxidized by oxygen. Its oxidation with organic peroxide compounds is now a subject of considerable interest. The present work was devoted to a study of the reaction of hexaethyldilead with cumene hydroperoxide and with p-diisopropylbenzene dihydroperoxide.

Hexaethyldilead (HEL) readily reacts with solutions of aralkyl hydroperoxides, even at 15-20°. At low initial concentrations (up to 0.3 mole/liter) of the reacting substances in n-hexane, n-nonane, or trichlorbenzene and in the absence of an excess of hydroperoxide, this reaction takes place with the formation of a colorless, crystalline precipitate. From the lead content and by titration of an aqueous solution of this precipitate, it was identified as triethyllead hydroxide. This compound is formed by reaction of HEL with, for example, cumene hydroperoxide:

$$(C_2H_5)_3Pb - Pb (C_2H_5)_3 + C_6H_5 (CH_3)_2COOH \rightarrow \tag{1}$$
$$\rightarrow (C_2H_5)_3PbOH + (C_2H_5)_3PbOC (CH_3)_2C_6H_5$$
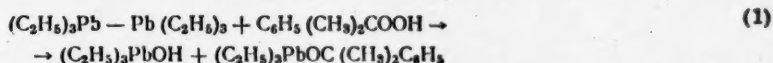
According to Reaction (1), the conversion of 1 mole of HEL results in the formation of 1 mole of triethyllead hydroxide. This compound should precipitate rather completely, since, according to the literature [1], its solubility in hydrocarbons and their chlorinated derivatives is very low. In actuality, we found the precipitation to be significantly less than quantitative. Moreover, if the reaction of HEL with cumene hydroperoxide was carried out in the presence of an excess of the latter, no triethyllead hydroxide at all precipitated. The results of experiments on the effect of the ratio of initial concentrations of reactants in hexane on the amount of triethyllead hydroxide precipitating are presented in Table 1.

TABLE 1

Yield of Triethyllead Hydroxide (in % of HEL). Initial Concentration of HEL, 0.115 mole/liter; Temperature, 14-16°

Mole ratio HEL to hydroperoxide	In precipitate, %	Extracted from solution, %	Total, %
2 : 1	19	30	49
1 : 1	24	65	89
2 : 3	19	99	119
1 : 2	8	135	143
1 : 3	0	182	182

It was found that if the reaction mixture was washed after separation of the precipitate, the aqueous layer contained a considerable amount of triethyllead hydroxide. This was probably due to hydrolysis of more complex compounds formed during the reaction of HEL with hydroperoxide.

As may be seen from an inspection of Table 1, with an increase in the concentration of hydroperoxide with respect to HEL, the yield of solid triethyllead hydroxide decreased, and the yield of hydroxide extracted from solution increased; moreover, the total yield of this organolead base increased. On the basis of these data, we assume that Reactions (2) and (3) take place in the reaction mixture successively with Reaction (1):

$$(C_2H_5)_3PbOH + C_6H_5(CH_3)_2COOH \rightleftarrows (C_2H_5)_3PbOOC(CH_3)_2C_6H_5 + H_2O \qquad (2)$$

$$(C_2H_5)_3PbOC(CH_3)_2C_6H_5 + C_6H_5(CH_3)_2COOH \rightarrow$$
$$\rightarrow (C_2H_5)_3PbOOC(CH_3)_2C_6H_6 + C_6H_5(CH_3)_2COH \qquad (3)$$
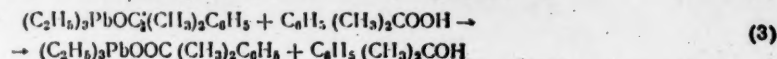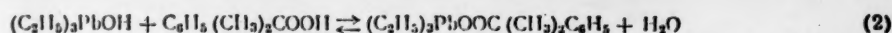
Reaction (2) is accompanied by the formation of water, which separated as drops on the walls of the reaction vessel. This water was identified by the formation of hydrated copper sulfate. We made an attempt to isolate the triethyllead cumyl peroxide [triethyllead α, α-dimethylbenzyl peroxide]. For this purpose, Reaction (2) was carried out at 14-16° with equivalent amounts (0.2 mole/liter) of triethyllead hydroxide and cumene hydroperoxide. After 15-18 hours, the reaction mixture was filtered to remove the water formed during the reaction, and the solvent (hexane) was then distilled under reduced pressure (1-2 mm Hg) at a temperature not above 16°. A gold-colored liquid, which readily underwent thermal decomposition, remained in the reaction vessel. When heated for a short time at 70-80°, this liquid acquired a red-brown color, and at 90°, it decomposed rapidly with the evolution of a gas and the formation of a brown residue. Comparatively rapid decomposition, even at room temperature, took place during storage of the peroxide compound in a sealed ampoule. This material was readily hydrolyzed by water with the formation of triethyllead hydroxide and cumene hydroperoxide in quantitative yield, which indicates that Reaction (2) is reversible. It reacted vigorously with glacial acetic acid with the formation of triethyllead acetate.

TABLE 2

Yield of $(C_2H_5)_3PbOH$ (in %). Experiment Temperature, 40°

HEL conc.		Reaction time, hours						
in TEL, wt. %	in reaction mixture, mole/l	1	2	3	4	5,5	6	8
0,73	0,01	64	—	84	—	91	—	94
1,41	0,02	76	84	89	—	—	93	—
2,79	0,04	82	39	—	90	—	91	—
6,70	0,04	81	85	—	87	—	87	—

TABLE 3

Yield of $C_2H_5)_3P$ OH (in %). Concentration of HEL in TEL, 0.73 Wt. %; Concentration in Reaction Mixture, 0.01 Mole/Liter

T°.C	Reaction time, hours											
	1	2	3	4	5,5	6	8	9	12	15	18
30	55	—	73	—	—	85	—	89	93	94	96
40	64	—	84	—	91	—	94	—	—	—	—
50	82	91	—	97	—	102	—	—	—	—	—

We next carried out the reaction of triethyllead hydroxide with p-diisopropylbenzene dihydroperoxide. For this purpose, weighed portions of the solid starting materials were placed in a small flask, to which hexane was then added. In spite of the fact that both reactants are difficultly soluble in hexane, when the reaction mixture was vigorously agitated at room temperature, the solid material rapidly went into solution, and water was simultaneously formed. This indicates that the following reaction occurred:

$$2(C_2H_5)_3PbOH + C_6H_4[C(CH_3)_2OOH]_2 \rightleftarrows [(C_2H_5)_3PbOO(CH_3)_2C]_2C_6H_4 + 2H_2O \qquad (4)$$
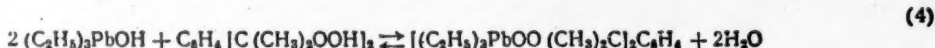
The reaction mixture was filtered, and the solvent was then distilled under reduced pressure (1-2 mm Hg) at a temperature of 14-16°. The resulting precipitate was washed with a small amount of hexane. The resulting purified preparation was analyzed electrolytically for lead content. It was found that 90% of the preparation consisted of a basic material, $[(C_2H_5)_3PbOO(CH_3)_2C]_2C_6H_4$. This compound was very readily soluble in all of the solvents used (benzene, toluene, trichlorobenzene, acetone, ether, and petroleum ether), and was difficultly soluble in cold hexane or nonane. When heated in a sealed capillary, it melted at 40-42° with the formation of a transparent liquid, which, on further heating, gradually darkened and rapidly decomposed, at 105°, with the separation of a tarry material and a brown solid. When stored in air, the organolead peroxide compound comparatively rapidly turned yellow and decomposed.

When this organolead peroxide compound was vigorously agitated with water, reaction occurred accompanied by the separation of a white precipitate, which was identified as para-diisopropylbenzene dihydroperoxide by its melting point and by determination of the active hydrogen. By iodometric titration, it was found that this material comprised 95-96% of the theoretical amount of dihydroperoxide. These results are convincing proof

that Reaction (4) is also reversible. Thus, the present work has demonstrated the formation of organolead peroxide compounds having the formulas $(C_2H_5)_3PbOOC(CH_3)_2C_6H_5$ and $n-(C_2H_5)_3 \cdot PbOOC(CH_3)_2C_6H_4(CH_3)_2COOPb(C_2H_5)_3$. These compounds are analogous in structure to the previously prepared organotin [2] and organogermanium [3] compounds, which are also readily hydrolyzed by water or dilute acids. Our investigation of the oxidation of HEL by cumene hydroperoxide in the presence of tetra-ethyllead (TEL) is also of considerable interest. We carried out several series of experiments in which a mixture of HEL and TEL was subjected to oxidation by hydroperoxide. The results of these experiments are presented in Tables 2 and 3.

In these experiments, the mixture of HEL and TEL, diluted with a two-fold volume of nonane, was placed in ampoules (10 ml in each ampoule), and the ampoules were then sealed and placed in a thermostatted bath. The mixture with the highest concentration of HEL (6.7%) was diluted 5-fold. After a predetermined time, the ampoules were removed, their contents were carefully washed with water, and the amount of triethyllead hydroxide formed was determined by titration of the aqueous solution with acid. The yield of hydroxide is expressed in per cent of the amount calculated from theory assuming that 2 moles of triethyllead hydroxide were formed from 1 mole of HEL. All of the experiments were carried out with hydroperoxide concentrations which exceeded the HEL concentration by a factor of 5. As may be seen from a consideration of Tables 2 and 3, the oxidation of mixtures of HEL and TEL by cumene hydroperoxide proceeded at 30 and 40° with yields of triethyllead hydroperoxide of 87-96%. This indicates that TEL is not oxidized under the conditions of these experiments. At higher reaction temperatures (beginning at 50°), the reaction of TEL with hydroperoxide takes place at an appreciable rate. These results were confirmed by special experiments carried out with TEL (free of HEL) and cumene hydroperoxide.

The results of our experiments suggest that the oxidation of HEL by cumene hydroperoxide can be used for the determination of the content of this organolead compound in TEL. Organolead peroxide compounds can react with HEL:

$$(C_2H_5)_3PbOOC(CH_3)_2C_6H_5 + (C_2H_5)_3Pb - Pb(C_2H_5)_3 \rightarrow \qquad (5)$$
$$\rightarrow (C_2H_5)_3PbOPb(C_2H_5)_3 + (C_2H_5)_3PbOC(CH_3)_2C_6H_5$$
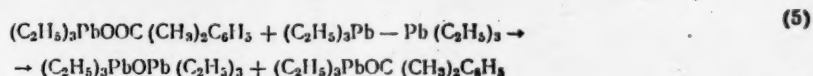
We carried out this reaction in hexane solution at 14-16°. After 4-5 days, colorless crystals separated from the reaction mixture. These crystals were washed with a small amount of hexane and dried at 14-16° under reduced pressure (1-2 mm Hg), after which they were readily soluble in water and difficultly soluble in ether and acetone. Analysis of this substance by titration of its aqueous solution with acid showed that it was either triethyllead hydroxide or bis(triethyllead) oxide $-(C_2H_5)_3PbOPb(C_2H_5)_3$. From a comparison of the solubility in acetone of triethyllead hydroxide with that of the compound isolated by us, and also from a comparison of their thermal stabilities, we came to the conclusion that this crystalline material was probably triethyllead oxide. HEL also very readily reacts at room temperature with acyl peroxides. For example, the reaction with benzoyl peroxide in benzene solution proceeds according to the equation:

$$(C_2H_5)_3Pb - Pb(C_2H_5)_3 + C_6H_5\overset{O}{\overset{\|}{C}} - O - O\overset{O}{\overset{\|}{C}} - C_6H_5 \rightarrow 2 \ (C_2H_5)_3PbO\overset{O}{\overset{\|}{C}} - C_6H_5 \qquad (6)$$
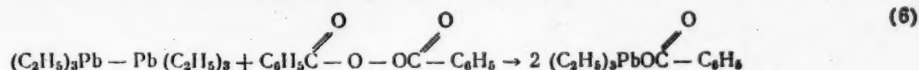
After only a few minutes, the peroxide disappeared from the reaction mixture, and partial separation of triethyllead benzoate as well-formed crystals occurred; this substance was identified by melting point (127°) and by mixed melting point with a known sample of the substance (m. p. according to reference [4], 127°).

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OXIDATION OF DIALDEHYDIC CELLULOSE
WITH NITROGEN OXIDES

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Oxidation of dialdehydic cellulose (II) with sodium chlorite [1] leads to the formation of a dicarboxycellulose with carboxyl groups at the second and third carbon atoms (III).
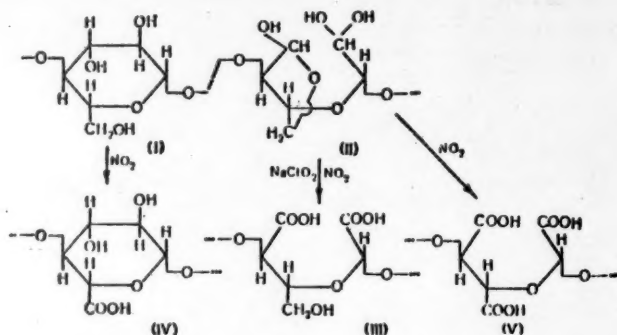
During the course of this reaction, a part of the oxidation product goes into solution owing to oxidative-hydrolytic decomposition [1], and part of the aldehyde groups at C_2 are incompletely oxidized [2]. Therefore, fibrous hydroxycellulose products (III) with a carboxyl group content not in excess of 20% by weight are obtained. By oxidizing dialdehydic celluloses with nitrogen oxides we obtained carboxycelluloses with a fibrous structure and with a carboxyl group content of up to 50%. We have provisionally named these hydroxycellulose products tricarboxycelluloses [3].

The present communication reports data on the rate of oxidation of aldehyde groups in dialdehydic celluloses by nitrogen oxides during the preparation of tricarboxycelluloses; data on the chemical composition of tricarboxycelluloses are also presented. The preparations of dialdehydic cellulose were obtained by oxidation of cotton cellulose with sodium periodate [1]. Oxidation of these dialdehydic celluloses with nitrogen oxides was carried out under static conditions at room temperature over a period of 24-72 hours. The rate of oxidation of the dialdehydic celluloses by nitrogen oxides was determined by the decrease in aldehyde group content and by the increase in the number of carboxyl groups. The contents of aldehyde and carboxyl groups (total and uronic) were determined by well known methods [4-6]. Curves are presented in Fig. 1 showing the comparative rates of oxidation by nitrogen oxides of a cotton cellulose and of a dialdehydic cellulose with an aldehyde group content of 24.5%.

The curves of Fig. 1 show that after the first 24 hours, oxidation proceeds chiefly with the formation of units of structure III (Fig. 1, Curve 2), through units of structure IV are formed in small amount (Fig. 1, Curve 3). The presence of aldehyde groups has no appreciable effect on the rate of oxidation at C_6 in 1, 5-anhydroglucose units (structure IV); this is confirmed by a comparison of the data on the oxidation of the dialdehydic and the original
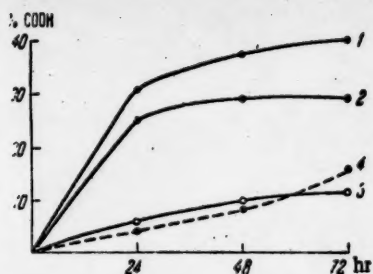
Fig. 1. Oxidation rate curves for a dialdehydic cellulose (1, 2, 3) and cellulose (4): 1—total COOH group content; 2—nonuronic COOH groups at C_2 and C_3; 3—uronic COOH groups; 4—uronic COOH groups.

TABLE 1

Relationship Between the Content of Aldehyde Groups and the Carboxyl Groups Formed from Them

Preparation No.	CHO group content, %	Nonuronic COOH group content, %	Oxidation, % of theoretical
25	18,2	25,9	109,3
19	24,7	34,5	107,0
20	29,5	39,4	103,0
21	28,3	43,4	118,0
28	36,9	49,5	103,0

cotton celluloses (Fig. 1, Curves 3 and 4). It can be seen from a comparison of Curves 2, 3, and 4 that the rate of oxidation of aldehyde groups at C_2 and C_3 is significantly greater than the rate of oxidation of hydroxyl groups at C_6. Data on the oxidation by nitrogen oxides of dialdehydic celluloses with different aldehyde group contents are presented in Table 1. It follows from the data of Table 1 that aldehyde groups at C_2 and C_3 are completely oxidized to yield structural units III, since the carboxyl group content in the final product is somewhat greater than theoretical (Table 1).

TABLE 2

Content of Total, Uronic, and Nonuronic Carboxyls in Tricarboxycelluloses

CHO group content in original dialdehydic cellulose, %	COOH group content after oxidation by nitrogen oxides, %			U/C
	total	uronic	non-uronic	
18,20	34,00	8,10	25,90	0,30
24,70	40,80	6,30	34,50	0,20
28,30	47,50	4,10	43,40	0,10
36,90	51,80	2,30	49,50	0,05

From a comparison of the uronic (U) and nonuronic (C) carboxyl group contents it follows that during the action of nitrogen oxides on a dialdehydic cellulose, oxidation at C_6 proceeds chiefly in unsubstituted glucose units. In this case, relatively less uronic carboxyls will be formed as the amount of units having structure II increases; i. e., the ratio U/C will decrease, as may be seen from the data of Table 2.

From a comparison of the uronic (U) and nonuronic (C) carboxyl group contents it follows that during the action of nitrogen oxides on a dialdehydic cellulose, oxidation at C_6 proceeds chiefly in unsubstituted glucose units. In this case, relatively less uronic carboxyls will be formed as the amount of units having structure II increases; i. e., the ratio U/C will decrease, as may be seen from the data of Table 2.

From data on the nonuronic and uronic carboxyl group contents per 100 elemental units of the tricarboxycellulose molecule it was found that, on the average, a total of 100 glucose units was oxidized (Table 3). From this it may be concluded that all glucose units are oxidized; i. e., the unit contains carboxyl groups in the 2, 3, or 6 positions. That it was not possible to detect glucose chromatographically in the hydrolysis products of the tricarboxycelluloses (with the exception of the less-oxidized Sample 25) confirms this conclusion.

TABLE 3

Number of Structures III and IV Per 100 Elemental Units

Prepara-tion No.	Structure		Sum of III and IV
	III	IV	
15	55	32	87
19	74	25	99
20	84	22	106
21	93	16	109
28	107	9	116

TABLE 4

Theoretical and Experimentally Determined Carboxyl Group Contents in the Elemental Unit of Tricarboxycellulose

CHO group content in original preparation, %	Nonuronic COOH group content in tricarboxy-cellulose, %		Deviation from theo-retical, %
	calculated	found experimentally	
18,2	23,7	25,9	2,2
24,7	32,1	34,8	2,7
28,3	36,8	43,4	6,6
36,9	48,1	49,5	1,4

Consideration of the data on the relationships between the amounts of uronic and nonuronic carboxyl groups and the total carboxyl groups suggests that, in addition to units having the structures III and IV, the tricarboxycellulose molecule probably also contains units having the structure V. Indeed, in the case of oxidation of structure II to III and I to IV, the total amount of carboxyls must equal the sum of the uronic carboxyls and those at C_2 and C_3, which are formed by oxidation of the aldehyde groups in the original dialdehydic cellulose. The data of Table 4 show that such an equality does not exist.

Using the data of Table 4, it was calculated that the number of units of structure V is approximately 10-15 per 100 elemental units. On the basis of the experimental data presented above, the chemical structure of the tricarboxycelluloses prepared can be represented by the following formula:
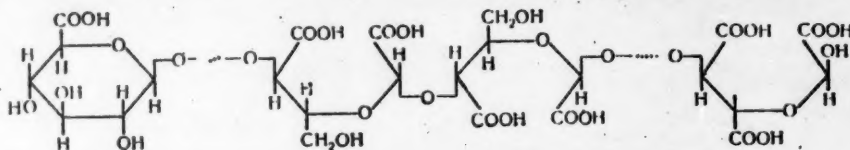
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PERFLUORODIENES

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In 1951, Haszeldine reported the telomerization of tetrafluoroethylene with iodine with the formation of α, ω-diiodoperfluoroalkanes. This work, which had as its aim the preparation of bifunctional derivatives of perfluoroalkanes, excited great interest; however, this reaction did not make this interesting type of compounds available since the conversion was low, and the mixture of telomerization products was difficult to resolve. Moreover, the inability of the CF_2I group to undergo heterolytic reactions greatly limits the possible conversion of the diiodides to derivatives of other types.

In contrast to Haszeldine's reaction, the method developed by us, telomerization of tetrafluoroethylene with 1, 2-dichloroiodotrifluoroethane, is easily controlled and results in a high yield of a mixture of telomers from which α, ω-perfluorodiolefins can be obtained by a series of ordinary operations. The telomerization is considerably facilitated by the use of benzoyl peroxide.

$$n \cdot CF_2 = CF_2 + CF_2Cl - CFClI \rightarrow CF_2Cl - CFCl \, (CF_2 - CF_2)_{n-1} \, CF_2CF_2I$$
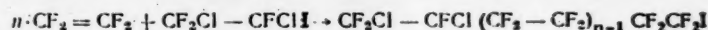
Using this method, we obtained good yields of the pure, individual telomers having $\underline{n}$ equal to 0, 1, and 2. As in all cases, the relative amounts of the individual telomers in the reaction products depends on the reaction conditions and the amount of telogen used. In all experiments, the amount of benzoyl peroxide used was 1% of the 1,2-dichloroiodoperfluoroethane.

α, β, ψ, ω-Tetrachloroperfluoroalkanes were obtained by the action of metallic zinc on a solution of the telomers in methylene chloride in the presence of acetic anhydride, and these were converted to α, ω-perfluorodienes by dechlorination with zinc in acetic acid:

$$2CF_2Cl - CFCl \, (CF_2 - CF_2)_n I \xrightarrow{Zn}{CH_2Cl_2} CF_2Cl - CFCl \, (CF_2 - CF_2)_{2n} CFCl - CF_2Cl \rightarrow$$

$$\xrightarrow{Zn}{CH_3COOH} CF_2 = CF \, (CF_2 - CF_2)_{2n} CF = CF_2.$$
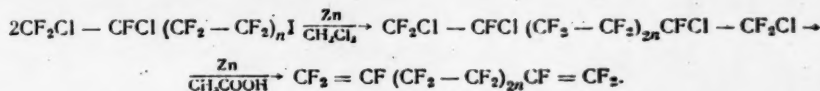
Perfluoro-1, 7-octadiene and perfluoro-1, 11-dodecadiene were prepared by this method. The preparation of perfluorodiolefins opens up the possibility of synthesizing perfluorinated dicarboxylic acids and other bifunctional compounds as well as the possibility of preparing polymers of the type of polyesters, polyamides, polyurethans, etc.

EXPERIMENTAL

Telomerization of tetrafluoroethylene with 1, 2-dichloroiodoperfluoroethane. 200 g (0.72 mole) of 1, 2-dichloroiodoperfluoroethane and 2 g of freshly precipitated benzoyl peroxide were charged to a 250-ml rotating steel autoclave. The autoclave was purged with dry nitrogen, cooled to $-60°$, and evacuated; 14 liters (0.7 mole) of tetrafluoroethylene was condensed in the autoclave and heated, with agitation, at $130°$ for 4 hours. The autoclave and contents were cooled, the unreacted tetrafluoroethylene was transferred to a gas holder (5 liters), and the remaining material was distilled in a column (17 theoretical plates); the following fractions were obtained:

I. 108 g of unreacted 1,2-dichloroiodoperfluoroethane; b. p. 47°/150 mm; 99-102°/760 mm.

II. 72 g of 1, 2-dichloro-4-iodoperfluorobutane; yield, 57% calculated on the 1, 2-dichloroiodoperfluoroethane reacted; b. p. 66°/67 mm; n_D^{20} 1.4046; $d_{\frac{20}{0}}$ 2.137. MR: found, 43.43; calculated 43.18. Mol. wt.: found, 374; calculated, 379.

$$\begin{array}{llll} & \text{Found \%:} & \text{C } 12.44; \; 12.08; & \text{F } 36.21; \; 35.69 \\ \text{C}_4\text{F}_7\text{Cl}_3 & \text{Calculated \%:} & \text{C } 12.68; & \text{F } 35.11 \end{array}$$

III. 75.5 g of 1, 2-dichloro-6-iodoperfluorohexane; yield, 24% calculated on the 1, 2-dichloroiodoperfluoroethane reacted; b. p. 81-82°/35 mm; n_D^{20} 1.3830; $d_{\frac{20}{0}}$ 2.097. MR: found, 53.30; calculated, 53.00. Mol. wt.: found, 479.5; calculated, 479.

$$\begin{array}{llll} & \text{Found \%:} & \text{C } 14.49; \; 14.72; & \text{F } 44.07; \; 43.28 \\ \text{C}_6\text{F}_{11}\text{Cl}_3 & \text{Calculated \%:} & \text{C } 15.05; & \text{F } 43.64 \end{array}$$

5 g of a thick, crystallizable mass (a mixture of higher telomers) remained in the distillation flask. Under these same conditions, the following were obtained from 93 g (0.3 mole) of 1, 2-dichloroiodoperfluoroethane, 1 g of benzoyl peroxide, and 14 liters (0.7 mole) of tetrafluoroethylene:

1. 53 g of unreacted 1,2-dichloroiodoperfluoroethane.

2. 21 g of 1, 2-dichloro-4-iodoperfluorobutane; yield, 39% calculated on the 1, 2-dichloroiodoperfluoroethane reacted.

3. 15.8 g of 1, 2-dichloro-6-iodoperfluorohexane; yield, 23%.

4. 20 g of 1, 2-dichloro-8-iodoperfluorooctane; yield, 24%; b. p. 82°/3 mm. Mol. wt.: found, 569; calculated, 579.

$$\begin{array}{llll} & \text{Found \%:} & \text{C } 16.69; & \text{F } 49.11 \\ \text{C}_8\text{F}_{15}\text{Cl}_3 & \text{Calculated \%:} & \text{C } 16.58; & \text{F } 49.22 \end{array}$$

5. 20 g of a mixture of unidentified higher telomers.

TABLE 1

Ratio of $\text{CF}_2\text{ClCFClI}$ to $\text{CF}_2=\text{CF}_2$	Reac. temp. °C	Reac. time, hr.	Yield of telomers, %*		
			$n=0$	$n=1$	$n=2$
4 : 1	90	8,5	53,1		
2 : 1	135	4	62,4	19,8	
1 : 1	130	5	57,0	24,0	4,5**
1 : 2	130	4	39,2	23,0	52,7**

* Calculated on the 1, 2-dichloroiodoperfluoroethane reacted.
** Calculated on the total weight of telomers.

1, 2, 7, 8-Tetrachloroperfluorooctane. To a mixture of 10.0 g (0.15 mole) of granulated zinc, 34.0 g (0.3 mole) of acetic anhydride, and 50 ml of dry methylene chloride was gradually added, with agitation, 56.9 g (0.15 mole) of 1, 2-dichloro-4-iodoperfluorobutane. The reaction was exothermic. The addition of the iodide was controlled so that the temperature of the reaction mixture was maintained at about 40°. After the iodide had been added, the reaction mixture was stirred for 6 hours at 40°, and 100 ml of water was then added as the mixture cooled; the lower layer was separated, washed with water, dried with magnesium sulfate, and distilled using a dephlegmator. 29.9 g of 1, 2, 7, 8-tetrachloroperfluorooctane was obtained; yield, 80%; b. p. 67-68° per 3 mm; n_D^{20} 1.3604; $d_{\frac{20}{0}}$ 1.840. MR: found, 60.19; calculated, 60.56. Mol wt.: found, 505; calculated, 503.92.

$$\begin{array}{llll} & \text{Found \%:} & \text{C } 19.61; & \text{F } 52.96 \\ \text{C}_8\text{F}_{14}\text{Cl}_4 & \text{Calculated \%:} & \text{C } 19.06; & \text{F } 52.79 \end{array}$$

1, 2, 11, 12-Tetrachloroperfluorododecane. To a mixture of 13.5 g (0.2 mole) of granulated zinc, 41 g (0.4 mole) of acetic anhydride, and 150 ml of dry methylene chloride was gradually added, with stirring, 96 g

(0.2 mole) of 1, 2-dichloro-6-iodoperfluorohexane in 50 ml of methylene chloride. The reaction conditions were those described for the preceding experiment. The zinc was filtered from the reaction products, which were then dried and distilled. 54 g of 1, 2, 11, 12-tetrachloroperfluorododecane was obtained; yield, 77%; b.p. 116°/3 mm; m. p. 68-68.5° (from CCl_4).

$$\text{Found \%:} \quad \text{C } 20.82; \quad \text{F } 59.33$$
$$C_{12}F_{22}Cl_4. \text{ Calculated \%:} \quad \text{C } 20.46; \quad \text{F } 59.37$$

Perfluoro-1, 7-octadiene. To a four-necked flask, fitted with a stirrer, a reflux condenser, a dropping funnel, and a thermometer, was charged 60 ml of glacial acetic acid, 20 ml of acetic anhydride, two drops of concentrated sulfuric acid, and 20 g of granulated zinc.

This mixture was heated to the boiling point of acetic acid, and 25 g of 1, 2, 7, 8-tetrachloroperfluorooctane was gradually added with stirring. The boiling point of the reaction mixture gradually decreased to 103°. The reflux condenser was replaced by a dephlegmator, and the reaction products were distilled until the temperature of the reaction mixture had again increased to 115°. 7 g of zinc was added to the remaining material, and heating was continued for another 3 hr; the reaction product was then again distilled until the material distilling over no longer stratified when diluted with water. The distillates were combined, washed with water and with a solution of sodium bicarbonate, and dried with magnesium sulfate. Distillation with a dephlegmator gave 13.1 g of perfluoro-1, 7-octadiene; yield, 72.5%; b. p. 105-107°; n_D^{20} 1.3020; d_{20}^{20} 1.695. MR: found, 40.52; calculated, 40.18.

$$\text{Found \%:} \quad \text{C } 26.72; \quad \text{F } 73.24$$
$$C_8F_{14}. \text{ Calculated \%:} \quad \text{C } 26.54; \quad \text{F } 73.47$$

Perfluoro-1, 11-dodecadiene. A mixture of 250 ml of acetic acid, 50 ml of acetic anhydride, two drops of concentrated sulfuric acid, 40 g of granulated zinc, and 104 g of tetrachlorododecane was stirred at the boiling point for 6 hours; it was then cooled, 200 ml of water was added gradually, the lower layer was separated, washed with water, with a solution of sodium bicarbonate, and again with water, and dried with magnesium sulfate. Distillation with a good dephlegmator gave 43 g of perfluorododecadiene; yield, 52%; b. p. 181-182°; n_D^{20} 1.3115; d_{20}^{20} 1.826. MR: found, 59.99; calculated, 59.78.

$$\text{Found \%:} \quad \text{C } 25.60; \quad \text{F } 72.44$$
$$C_{12}F_{22}. \text{ Calculated \%:} \quad \text{C } 25.62; \quad \text{F } 74.38$$

The distillation residue was again dechlorinated.

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CONTRIBUTION TO THE PROBLEM OF THE INTERACTION
OF QUATERNARY SALTS OF 2-METHYLBENZOTHIAZOLE
AND ITS DERIVATIVES WITH ESTERS
OF ORTHO CARBOXYLIC ACIDS

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The condensation of quaternary salts of heterocyclic compounds substituted at the α- and γ-methylenic carbon atoms (I) with esters of ortho carboxylic acids in pyridine solution [1-3] or in acetic anhydride [1], nitrobenzene [4] or other solvents [5] is a general method for the preparation of carbocyanine dyes (II), for example:
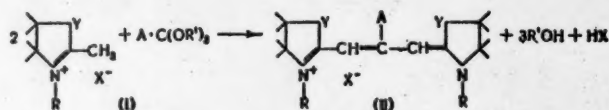
where Y is O, S, Se, NR_1, CH = CH, etc.; A is H, alkyl, or aryl; R and R_1 is alkyl or aryl; R is alkyl; and X is an anion.

The less the basicity of the quaternary salt [6, 7] and the higher basicity of the reaction medium [7], the more readily the dyes are formed. However, in a number of cases, particularly when the ortho esters used are those of orthoacetic and higher acids, the carbocyanines are formed in lower yield and sometimes are not formed at all. The alkyl group at the nitrogen atom and the anion of the quaternary salt have a considerable effect on the yield of the dye (see, for example, references [2, 3, and 8]).

The mechanism of this interesting reaction is not clear at present. It has been proposed that a reaction between equimolar amounts of the quaternary salt of the corresponding methylene base and the ortho ester (or the hypothetical product of its interaction with the acid split from the quaternary salt [1]) occurs first with the formation of the quaternary salt of the β, β-dialkoxyalkyl (III) [1, 9] or β-alkoxyalkenyl (IV) [9, 10] derivative of the heterocyclic base. These compounds then react with a second molecule of the quaternary salt (I) (or the methylene base) to form the dye.

However, it has not been possible to isolate compounds (III) and (IV) during this reaction [11]. It has been shown only that 2-acylmethylene-3-alkylbenzothiazoles (V) are formed during the reaction, in addition to carbocyanines, from quaternary salts of 2-methylbenzothiazole and its derivatives (V) [9, 12].
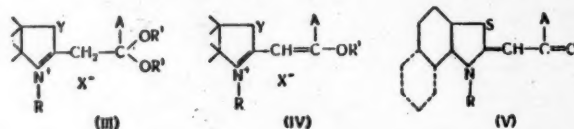
With the aim of studying this reaction, we have investigated the interaction of 2-methylbenzothiazole ethiodide and of 2-methyl-β-naphthothiazole methyl- anu ethyl-p-toluenesulfonates with the triethyl esters of orthoacetic and orthopropionic acids at 100-140°; the reactions were carried out both without a solvent and in solution in the anhydrides of the orthocarboxylic acids.

Moreover, when the reaction was carried out in the absence of a solvent, in addition to the corresponding carbocyanines, rather difficultly soluble compounds with the properties of quaternary salts were isolated as the iodides (the yield from 2-methylbenzothiazole ethiodide was 20-35% of theoretical and 5-6% from the salts of 2-methyl-β-naphthothiazole). When heated in pyridine, these compounds were converted to the acylmethylene derivatives (V), while their reaction with 2-β-acetanilidovinylbenzothiazole ethiodide in alcohol containing $N(CH_2H_5)_3$ gave the 9-ethoxythiadicarbocyanines. The indicated properties show that these compounds are al-kiodides of 2-β-ethoxyalkenylbenzothiazoles and -β-naphtholes[13]; the mixtures with known samples showed no depression of the melting point. Thus, 2-β-ethoxypropenylbenzothiazole (colorless crystals with an m. p. of 151-152°) was obtained in a yield of 20% of theoretical from 2-methylbenzothiazole ethiodide (0.1 mole) and triethyl orthoacetate (0.02 mole; 6 hours at 130°), while 2-ethyl-β-naphthothiazole ethyl p-toluenesulfonate (2 hours at 135-140°) gave 2-β-ethoxypropenyl-β-naphthothiazole ethiodide (52% yield; slightly greenish plates with an m. p. of 164-166°).

Moreover, from the reaction mixtures were isolated the corresponding acylmethylene derivatives (V) (the yields in the cases cited above were 10 and 7% of theoretical), the formation of which can apparently be explained by thermal decomposition of the quaternary salts (IV). These same products were obtained by the interaction of the 2-methylbenzothiazole and 2-methyl-β-naphthothiazole salts indicated above with ortho esters in a medium of the anhydride of the corresponding carboxylic acid. In this case, the amount of dye formed was appreciably increased (to 32% of theoretical in the case of the 2-methyl-β-naphthothiazole derivatives). The reaction takes place even at 90-100°.

It is interesting that when 2-methyl-β-naphthothiazole ethyl p-toluenesulfonate (0.005 mole) was heated (2 hours at 95-100°) with triethyl orthopropionate (0.01 mole) in acetic anhydride (2.5 ml), a considerable amount of 2-acetylmethylene-3-ethyl-β-naphthothiazole (m. p. 182-184° [14]) was formed in addition to the products corresponding to the ortho ester. Similarly, the 2-propionylmethylene derivative (m. p. 120-121° [14]) was pre-pared from triethyl orthoacetate in propionic anhydride.

When heated under these same conditions with anhydrides of carboxylic acids, the indicated salt underwent practically no change; therefore, it is possible that the formation of these acylmethylene derivatives is associated with the interaction of the ortho ester with the acid anhydride and the formation of the mixed ester-anhydride (VI)[15]:

$$(R - CO)_2O + R_1C(OC_2H_5)_3 \rightarrow R - C - O - C(OC_2H_5)_2 + R - COOC_2H_5.$$

(VI)
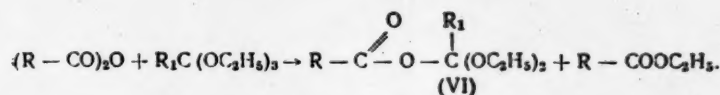
It may be assumed that compounds having the structure (VI) can react with salts (I) with the formation of both carbocyanines (like diethoxymethyl acetate [16]) and acylmethylene derivatives. We also investigated the products formed by refluxing a mixture of 2-methyl-β-naphthothiazole ethyl p-toluenesulfonate with triethyl orthopropionate in pyridine [9]. In this case, in addition to 3, 3', 9-triethyl-4, 5, 4', 5'-dibenzothiacarbocyanine and 2-propionylmethylene-3-ethyl-β-naphthothiazole [9], we also isolated two colorless substances which were neutral and had melting points of 173-174° and 73-74°; we also isolated, as the iodide, a small amount of a read-ily soluble quaternary salt (m. p. 152-156°), the properties of which differed from those of 2-β'-ethoxybutenyl-β-naphthothiazole (m. p. 165-166°).

The properties of the first of these compounds (formation of a secondary amine by refluxing with hydro-chloric acid, preparation of a substance with the properties of thiophenol by reduction with sodium sulfide) and the results of the chemical analysis of this compound show that it is bis(1-N-acetyl-N-ethyl-2-aminonapthyl) di-sulfide (VII). The investigation of the other two substances is being continued.

$$C_{28}H_{28}O_2N_2S_2. \quad \begin{array}{lll} \text{Found \%:} & \text{N } 5,86; \ 5,84; & \text{S } 13,28 \\ \text{Calculated \%:} & \text{N } 5,73; & \text{S } 13,12 \end{array}$$

(VII)
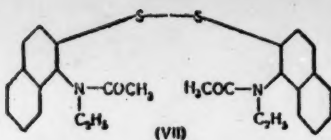
The amount of disulfide (VII) was appreciably increased when the quaternary salt was dissolved in pyridine, and the ortho ester was then added (the yield of carbocyanine was decreased by this procedure).

It was found that disulfide (VII) was formed in considerable yield when a solution of 2-methyl-β-naphtho-thiazole ethyl p-toluene-sulfonate in pyridine was refluxed (the yield was 37% after 6 hours). It is evident that cleavage of the thiazole ring in this salt proceeds considerably more easily than in the case of quaternary salts of 2-methylbenzothiazole (cf [17]). It has thus been shown that quaternary salts of 2-methylbenzothiazole and its derivatives react with esters of orthoacetic and orthopropionic acids when mixtures of the two are heated (without a solvent or in solution in the anhydrides of these acids) with the formation of quaternary salts of 2-β-alkoxy-alkenylbenzothiazoles (IV).

The question of whether these compounds (IV) are intermediate products or by products in the preparation of carbocyanine dyes by the condensation of quaternary salts (I) with esters of orthocarboxylic acids in pyridine [2, 3] requires further study, since they rapidly decompose under these conditions [13].

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INVESTIGATION OF REACTION EQUILIBRIA
IN THE REDUCTION OF BERYLLIUM OXIDE WITH CARBON
AT HIGH TEMPERATURES

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The interaction of beryllium oxide with carbon has been studied by a number of authors. Lebeau [1] and, later, other investigators [2, 3] have shown that beryllium carbide is obtained when beryllium oxide is reduced with carbon in air or in an inert atmosphere at high temperatures. Kroll and Schlechton [4], who studied the reduction of beryllium oxide under vacuum, found that reduction begins at 1315° C, and at 1500° C they found metallic beryllium in the condensate. M. V. Smirnov and N. Ya. Chukreev [5] used a potentiometric method to investigate the reaction $Be_s + 1/2CO_2 = BeO_s + 1/2C_{graf}$ in the temperature interval from 682 to 1040° C. The equilibrium in the system beryllium oxide — carbon was investigated in the present work by a manometric method over the temperature interval 1400-2000° C. The manometric method is the most suitable one for equilibria investigations in metal oxide — carbon systems at high temperatures. This method has been successfully used in a number of studies, for example, in investigations of the systems zirconium dioxide — carbon [6, 7] and silicon dioxide — carbon [8].

EXPERIMENTAL

The beryllium oxide was prepared by calcining beryllium hydroxide at 1100°. The latter was obtained by precipitation by ammonia from a solution of twice-recrystallized beryllium nitrate. Charcoal, de-ashed by treatment with hydrofluoric and hydrochloric acids, was used for the reduction. The starting materials were sieved to finer than 200 mesh and calcined under vacuum at 2000° C. Stoichiometric amounts of beryllium oxide and carbon were carefully mixed and pressed in a mold under a pressure of 300 kg/sq. cm.

The investigation of equilibria in the reaction

$$BeO_s + 3/2C_s \rightleftarrows 1/2Be_2C_s + CO_g \tag{1}$$
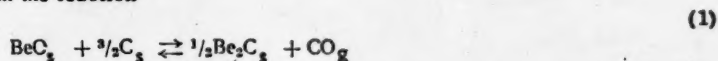
was carried out in a special apparatus which was similar in basic characteristics to that already described in [9]. The apparatus comprised a resistance furnace with a graphite heating element; the furnace was connected with a manometer, a vacuum system, and a system for collection and purification of the carbon monoxide. The furnace temperature was measured with an optical pyrometer having an accuracy of $\pm 10°$ C. The pyrometer was calibrated under the conditions of the experiment against a Mo—Mo/Al thermocouple which was introduced directly into the furnace. The thermocouple had previously been calibrated at the melting points of Rh, Pt, and Pd (by the "wire" method). The equilibrium pressure was measured with a McLeod gauge (at pressures below 6 mm) and with a U-type mercury manometer (at pressures above 6 mm). The furnace, together with the manometer, was placed in a thermostatted water bath, the temperature of which was controlled at $25 \pm 0.1°$ C. Prior to operation of the furnace, gases were desorbed from the heating element at a temperature 100-150° higher than the temperature of the

experiment to a pressure of $1 \cdot 10^{-5}$ mm Hg. The reaction mixture was charged to the working zone of the furnace, after desorption of gases from the heating element, without breaking the vacuum. However, it was noted that the reaction mixture contained a significant amount of adsorbed gases in spite of the preliminary heat treatment of the components. To remove the gases, the crucible containing the reaction mixture was heated for several minutes at the temperature of the experiment with the vacuum pumps in operation. After this, the furnace space was disconnected from the vacuum pumps, and the pressure in the system was measured. It was considered that equilibrium had been attained when the pressure remained constant for a period of 4-6 hours. A series of experiments was carried out using a dynamic method. The introduction of the predetermined amount of carbon monoxide into the system was carried out using proportioning valves. The equilibrium was approached from both sides in some experiments. The calculations were based on data obtained by both the static and dynamic (for the forward reaction) methods.
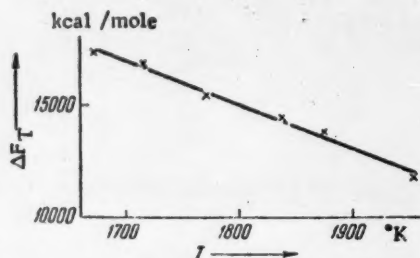
Fig. 1. Variation in the free energy change of reaction (1) with temperature.
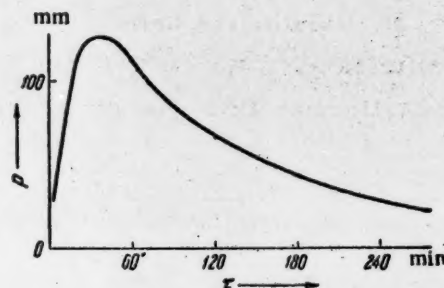
Fig. 2. Kinetic curve obtained at 2160° K.

The reaction products were subjected to chemical and x-ray phase analysis. Chemical analysis was carried out for C_t, Be_t, C_c, and C_f*.

C_t was determined by combustion of a weighed sample in a stream of oxygen. Be_t was determined as BeO by a gravimetric method after prolonged boiling of a weighed sample with sulfuric acid (1:1). The residual C_f was filtered using a quartz filter, and was determined by combustion.

C_c in the carbide was determined by hydrolysis of the carbide with concentrated alkali. The methane evolved during the hydrolysis was determined by combustion.

On the basis of these experiments, it was established that equilibrium pressure can be attained only in the temperature interval from 1700 to 1950° K. At these temperatures, the reaction products included beryllium carbide and unreacted beryllium oxide and carbon. At higher temperatures, the carbon monoxide pressure first reached a maximum and then sharply decreased; in some cases, it did not decrease to a definite value. The results of the pressure measurements in the temperature interval from 1700 to 1950° K and the free energies of the reaction are presented in Table 1.

TABLE 1

	Temperature, °K					
	1673	1716	1773	1837	1873	1953
Pressure in mm Hg	4,0	5,5	9,5	15,0	19,0	36,0
ΔF_T in cal /mole	17430	16793	15437	14315	13713	11824

When ΔF_T is plotted against T, the relationship is found to be linear (Fig. 1). This fact, as well as the analysis of the reduction products, allows us to conclude that in the temperature range of 1700-1950° K we are

*$\underline{t}$, $\underline{c}$, and $\underline{f}$ indicate total, combined, and free, respectively·

dealing with an equilibrium state corresponding to reaction (1); the dependence of ΔF_T (in the range 1700-1950°) on temperature for reaction (1) is expressed by the equation $\Delta F_T = 50864 - 19.22\ T$. Hence, ΔH_T (1700-1950°)= 50864, and ΔS_T (1700-1950°) = 19.92 e. u.

It has already been mentioned that, at high temperatures, a maximum was found in the kinetic curve. Such a curve, obtained at 2160° K, is shown in Fig. 2. Be_2C, BeO, and C were present in the reaction products corresponding to the rising portion of the curve. The reaction products corresponding to the falling portion of the curve consisted of almost pure carbon. The time during which the maximum pressure was maintained depended on the amount of reaction mixture used. This time was lower the less the amount of reaction mixture. A considerable amount of sublimate was found on the cool parts of the heating element. The sublimate was subjected to x-ray phase analysis, and lines corresponding to beryllium oxide and carbon were found; there were also a small number of weak lines which could not be assigned either to Be_2C or to C, Be, and BeO, and which, therefore, indicated the presence of some new phase. The vapor pressure of beryllium oxide is extremely low at 1950-2250° K [10], so that the appearance of a significant deposit of beryllium oxide cannot be explained by simple evaporation from the reaction zone. The probable mechanism of the reactions taking place in the range 1950-2250° K can be represented as follows. Very slight dissociation of the beryllium carbide begins at a temperature of 1950°.

$$Be_2C_s \rightleftarrows 2Be_g + C_s \qquad (2)$$

Extrapolation of the data of Pollock [11] indicates that the vapor pressure of beryllium over beryllium carbide is about 0.7 mm at 1950° K. In the presence of carbon monoxide, the following reaction takes place:

$$Be_g + CO \rightarrow BeO_s + C_s . \qquad (3)$$
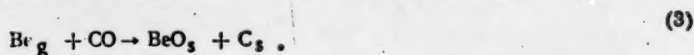
The latter reaction explains the appearance of beryllium oxide together with carbon on the cold parts of the heating element. Thus, beginning at 1950°, reactions (2) and (3) shift the equilibrium of reaction (1) to the right. Accordingly, the time during which the maximum pressure is maintained should depend on the amount of the reaction mixture.

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ON THE STRUCTURE OF SOME ENOL BETAINES
OF 5,5-DIMETHYL-1,3-CYCLOHEXANEDIONE

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By interacting 5,5-dimethyl-1,3-cyclohexanedione (dimedone) with iodobenzene, Gudrineitse and the present authors [1] obtained a new compound which they chose to call phenyldimedonyliodone and to which they assigned the structure of an inner salt (I).

$C_6H_5I^+$ (I) $C_6H_5I^+$ X^- (II)   (III) X^- (IV)
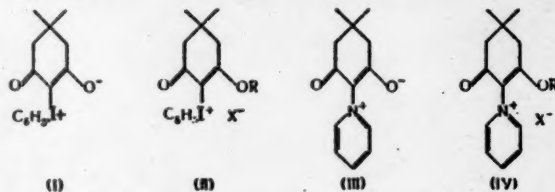
The present work was devoted to an investigation of the ultraviolet and infrared absorption spectra of iodone (I) and its derivatives. The absorption spectra of the enolate form of N-dimedonylpyridinium betaine (III) were investigated along with those of iodone. This compound is formed by cleavage of phenyl(O-ethyl-dimedonyl) iodonium fluoborate (II) ($R = C_2H_5$, $X = BF_4$) in the presence of pyridine after saponification of the ether group, and it bears a considerable resemblance in properties to iodone (forms adducts with acids; is readily alkylated). Similar betaines—derivatives of dibenzoylmethane—have been described by Kröhnke [2].

The major purpose of the spectroscopic investigation was to prove or disprove the enolate anion structure of these compounds. It is well known that the ultraviolet spectra readily distinguish the enolate anion form from the enol form by the bathochromic shift of the K-band [3], which for dimedone is 283 mμ and 258 mμ, respectively.

Recalling that substituents on the active methylene group also cause some bathochromic shift [4], it would be expected that the compounds investigated, (I) and (III), would absorb at about 300 mμ. On the contrary, both iodone and pyridinium betaine are characterized by a maximum at 260 mμ. In acid solutions, there was only a very slight shift, associated with the formation of the un-ionized forms (II) and (IV) (R = H), and the spectra corresponded to the enol ether derivatives (II) and (IV) ($R = C_2H_5$) (see Figs. 1 and 2).

The i. r. spectra also exhibited anomalies. In order to determine the characteristic frequencies of the enolate anion group, spectra were first taken of the sodium, tetramethylammonium, and diphenyliodonium salts of dimedone, both in the solid state and in solution in chloroform (except for the sodium salt); the spectrum of the sodium salt of 2-iododimedone was also obtained. It was found that the enolate anion system of dimedone is characterized by extremely intense adsorption in the region of 1510-1530 cm^{-1} (in the region of 1480-1500 cm^{-1} for the 2-iododimedone anion). On occasion, a second, less intense maximum or inflection was observed in the region of 1560-1570 cm^{-1}. By comparison with the frequencies of the enol forms of the dimedone ethers (1610 cm^{-1} for the double bond and 1660 cm^{-1} for the carbonyl group [5]), the enolate displays a considerable displacement of these frequencies, which is evidently associated with the formation of a symmetrical system with highly deformed carbonyl groups and double bond [6].
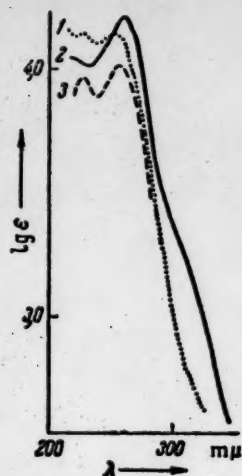
Fig. 1. U. v. absorption spectra of phenyldimedonyliodone. Methanol solvent: 1—phenyldimedonyliodone + HBF$_4$; 2—phenyldimedonyliodone; 3—phenyl(O-ethyldimedonyl)iodonium fluoborate.
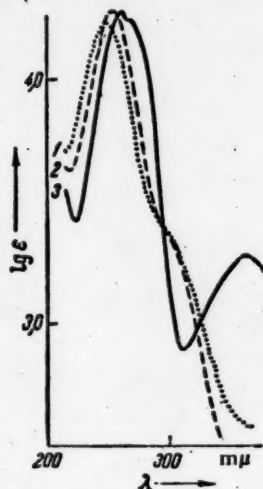
Fig. 2. U. v. absorption spectra of the enolate form of N-dimedonylpyridinium betaine. Methanol solvent: 1—N-dimedonylpyridinium betaine enolate + HCl; 2—O-ethyldimedonylpyridinium fluoborate; 3—N-dimedonylpyridinium betaine enolate.

It was found that iodone in chloroform, benzene, and alcohol solutions was characterized by only one very intense band in the double bond region; the band occurred at 1568, 1581, and 1563 cm^{-1} for the chloroform, benzene, and alcohol solutions, respectively. In the solid state, iodone had 2 intense bands in this region, at 1531 and 1602 cm^{-1}, and iodone hydrate was characterized by a very intense absorption at 1551 cm^{-1} in addition to low-intensity bands at 1599 and 1647 cm^{-1}. The adducts of iodone with hydrogen chloride (II, R = H, X = Cl), nitric acid (II, R = H, X = NO$_3$), and methylsulfuric acid (II, R = H, X = CH$_3$SO$_4$) showed the normal double bond and carbonyl frequencies at, respectively, 1586 and 1645 cm^{-1}, 1599 and 1661 cm^{-1}, and 1609 and 1655 cm^{-1}. Similarly, pyridinium betaine (III) in chloroform solution exhibited very intense absorption at 1539 cm^{-1} in addition to the weak absorption of the pyridinium ring at 1600 cm^{-1} and 1627 cm^{-1}. For this compound in the solid state, bands were found at 1544, 1600, and 1627 cm^{-1}. The betaine hydrate (III·2H$_2$O) had an intense band at 1514 cm^{-1} in addition to bands at 1594 and 1628 cm^{-1}. The perchlorate (IV) (R = H, X = ClO$_4$) was characterized by absorption of the normal enol system (1619, 1929*, and 1655 cm^{-1}).

Certain interesting conclusions follow from these data. Both in iodone and in pyridinium betaine, the dimedone group undoubtedly exists in the symmetrical anion form, except for iodone in the solid state where dimerization may possibly take place [7, 8]. But the distribution of electron density obviously differs to a considerable extent between the normal enolate anion and the anion form of the enol betaine. While in the normal enolate anion the electron density is greatest at the oxygen atoms, the most electronegative atoms, and the double bond is more of a one-and-a-half bond [6], in the enolates, under the influence of the positive charge directly around the active methylene group, the electron density is shifted toward the active methylene group. This changes the spectral characteristics: the double bond frequency is increased and the K-band in the u. v. spectra undergoes a hypsochromic shift. Consequently, the question arises as to whether the charge is localized on the oxygen or the carbon, a question which was considered some time ago by Krohnke [9]. Two possibilities exist for the representation of the structure of betaine enolates (remembering that the two oxygen atoms are equivalent):
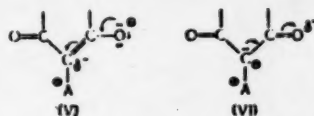
It might be assumed that localization of the electron charge would depend to a considerable extent on the nature of the substituent A and also on the solvent; however, the spectral properties are, to a great extent, satisfied by formula (V).

EXPERIMENTAL

Tetramethylammonium salt of dimedone. A solution of tetramethylammonium hydroxide was saturated with dimedone and evaporated under vacuum. The product was purified by reprecipitation from chloroform using absolute ether as the precipitant. Yellowish, extremely hygroscopic needles were obtained. M. p. 223° (with decomposition).

*On original copy, possibly should be 1629—Publisher's note.

Diphenyliodonium salt of dimedone. This was prepared similarly to the preceding salt. Reprecipitation from absolute alcohol using absolute ether as the precipitant gave yellowish, unstable crystals with an m. p. of 107-110°.

N-Dimedonylpyridinium betaine enolate (III). 22.9 g (0.05 mole) of the fluoborate (II, R = C_2H_5, X = BF_4) was stirred with 15 ml of pyridine at 20° for 10 hours. The crystals were suction filtered and treated with 7 ml of concentrated HCl on a boiling water bath for 5 hours; 10 ml of water and 13 g of potassium carbonate were then added, and the mixture was twice vigorously agitated with 200-ml portions of dichloroethane. Distillation of the dichloroethane gave 7 g (64%) of the betaine—dark yellow crystals (from a mixture of absolute alcohol and absolute ether) with an m. p. of 197-198°.

Light yellow needles of the dihydrate melted at 88-90°.

The perchlorate was obtained as yellowish prisms (from absolute alcohol and absolute ether) with an m. p. of 182-184°.

The spectra were obtained using SF-4 and IKS-12 instruments. The solid samples were examined as pastes in vaseline oil.

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THE MUTUAL EFFECT OF RARE EARTH ELEMENTS
DURING EXTRACTION WITH TRIBUTYL PHOSPHATE

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During a study of the equilibrium systems defining the extraction of uranyl nitrate with ether, one of us found that the uranyl nitrate in effect salts itself out of solution [1]; in particular, there was a threshold increase in extraction with concentration. During the extraction of thorium and aluminum nitrates with amyl alcohol, a mutual salting out effect was clearly observed [1] in which the agent which is usually thought of as the salting out agent $Al(NO_3)_3$ did not predominantly act as such in the aqueous phase, but was itself salted out from the organic phase by the substance being extracted $Th(NO_3)_4$.

TABLE 1

Element	E_2O_3 content in orig. solution, in %	Extraction, %	Conc. in aq. phase, %	Conc. in org. phase, %
Nd	Trace	14	(86)	(42)
	2	14	1,72	0,84
	5	14	4,3	2,1
	20	10	18,0	6,0
Sm	Trace	37	(63)	(111)
	2	35	1,3	2,1
	5	35	3,25	5,25
	20	16	16,8	9,6
Yb	Trace	93	(7)	(279)
	2	78	0,44	4,68
	5	58	2,1	8,7
	20	16	16,8	9,6

Note. Concentrations shown in parentheses are in % of the original aqueous phase. Values greater than 100% refer to concentration in the organic phase.

The mutual effect of the rare earth elements during extraction is of great interest, since they are always encountered together. The simplest case of such an effect which is of interest to us is the case in which extraction of an element changes with a change in its own concentration. We have studied the change in extraction with concentration for the extraction of neodymium, samarium, and ytterbium with tributyl phosphate (TBP); the medium was nitric acid (reagent grade). Direct determination of acidity in our experiments after the introduction of the rare earth salts showed the normality of the acid to be about 12. Throughout the remainder of this paper, we shall refer to this acid as concentrated HNO_3. In all experiments, the TBP was saturated with this acid prior to the extractions. With the aim of decreasing the change in concentration of the aqueous solution, the extractions were carried out at a volume ratio of aqueous to organic phase of 3/1. The following radioactive labels were used for analytical purposes: Nd[147], Sm[153], Yb[175], V[90], Ho[166]. The decrease in extraction with concentration has previously been noted for cerium (IV) (see [3]). The method has been described in greater detail in [8].

It is clear from Table 1 that in addition to the self-salting-out effect (increase in extraction with concentration), the rare earth elements also exhibit the reverse effect, which we propose to call the self-salting-in effect. The small salting-out effect observed for the rare earth elements would be expected in view of their significantly greater ionic radii (1.22-0.99 A) as compared to those of such recognized salting-out agents as Al^{+++}, Fe^{+++}, etc. (0.57, 0.67 A). The explanation of the salting-in effect is quite simple — it is the limited solubility of the rare earths in the organic phase. The greater the extraction, the sooner this peculiar salting-in effect must appear, as the ytterbium data persuasively show. On the contrary, constancy of extraction is retained for Nd and

TABLE 2

Didymium content ($\%\ E_2O_3$)	Nd, %	Sm, %	Y, %	Ho, %	Yb, %
0 *	14,0	37,0	85,6	78,6	92,6
2	14,0	39,0	83,9	77,0	90,5
5	14,0	34,1	81,2	76,9	86,7
20	8,9	30,3	70,0	70,2	89,6

* These data are in agreement with the literature values[7].

TABLE 3

Conc. of yttrium concentrate ($\%\ E_2O_3$)	Nd, %	Sm, %	Y, %	Ho, %	Yb, %
0	14	37	85,6	78,6	92,6
2	8,7	33	65,1; 79,9	52; 70,5	77; 83
5	7,1	18	45,6; 67,0	32; 55,6	59,4; 74,5
20	3,0	3	23,7; 14,0	149 —	19,7; 29,0

Sm from trace concentrations up to 5% and, probably, even somewhat higher; this has previously been pointed out [4]. This difference has important practical significance; the separation of yttrium rare earth elements should be more successful at low concentrations and should become worse at higher concentrations where their extraction becomes almost equal to that of the cerium group (even in the absence of a mutual effect).

In order to clarify this mutual effect properly, two series of experiments were undertaken. The first series should clarify the effect of concentration of cerium earths, in particular didymium earths (see [5] for preparation), on the extraction with tributyl phosphate of neodymium, samarium, yttrium, holmium, and ytterbium; the same nitric acid was used as the medium; the ratio of aqueous to organic phase was 3/1. The amount of extraction was determined by the use of radioactive labels (see above). According to spectroscopic data, the composition of the didymium was:

Nd	Pr	Sm	La	Eu	Gd	Dy	Er	Yb	Lu	V
55	17	3,7	7,0	0,72	0,7	<0,4	<0,1	0,04	0,04	<0,1%

The results of these experiments are shown in Table 2.

It is interesting that a 2-5% concentration of didymium had no effect in any of the cases, while a 20% concentration decreased the extraction of trace amounts for all of the rare earth elements investigated with the exception of ytterbium. Moreover, the effect successively decreased from neodymium to holmium. The lack of an effect on ytterbium and the noted decrease in the effect for Y and Ho suggests that the yttrium earths will have a greater effect on each other and, especially, on the cerium earths. Consequently, a second series of experiments was undertaken with an yttrium concentrate having the following composition (from spectroscopic data):

Nd	Pr	Sm	La	Eu	Gd	Tb	Dy	Er	Tu	Lu	V
2,5	0,7	2,4	4,3	<0,1	4,0	1,4	5,2	4,3	0,9	6,5	1,45%

Its effect on extraction under the same conditions and for the same active rare earth elements was studied (the following were introduced in trace amounts: Nd^{147}, Sm^{153}, Yb^{175}, V^{91}, Ho^{166}).

Even a 2% concentration of this added material had a very appreciable effect in all cases; the decrease in the extraction of, for example, neodymium was greater than for a 20% solution of its own salt. With a 5% concentration, the extraction of samarium was almost half of that for a 20% solution of its salt.

For ytterbium, the decrease in extraction was the same for equal concentrations of the added material and ytterbium salt. Since extraction of Y, Ho, and Yb was high, the concentration in the aqueous phase after extraction was significantly less, and a second extraction naturally showed an appreciable increase (values for the second extraction are also given in Table 3).

The regular decrease in the extraction of Y and Ho with concentration indicates that the presence of their salts in the added Y fraction should have a similar effect. Thus, the behavior noted above for ytterbium at different concentrations of its salts can be considered typical of all of the yttrium group.

The considerable effect of the yttrium concentrate indicates the mechanism of the effect, which is especially clear for neodymium and samarium at low extractions; the mechanism is salting out from the organic phase.

An experiment on the extraction of a trace amount of holmium in the presence of 0.2 g of didymium and 1.0 g of CeO_2 in 10 ml of solution is very indicative of the mechanism of the mutual effect. In the first extraction, about 75% of the Ce (IV)* went into the TBP, and the extraction of holmium was 40-68.8%; in the second and third extractions, even without the effect of Ce (IV), holmium extraction was 81 and 83.6%. The latter values are close to those which were obtained for a 2% solution of didymium alone.

In this same effect lies the reason for the equal extraction of Ce (IV) from solutions of the pure salt and from mixtures of all rare earth elements [3]; it determines the high quality of the Ce (IV) extract and, in particular, the lack of extraction of praseodymium in even trace amounts [3].

In addition to their scientific interest, the above facts also have a practical value:

1. Calculations of the total rare earth extraction based on the values of K_{dist} for the separate elements will not correspond to the actual extraction owing to the salting out effect, i. e., owing to the mutual effect. This explains the lack of correspondence between calculations based on K_{dist} and actual extractions, which has been pointed out in a number of articles [4].

2. The separation of rare earth elements at low concentrations will be easier than at high concentrations. It follows from all of the material presented above that it is necessary to separate the yttrium rare earth elements first, as these have the greatest effect. This gives a concentrate of them; the cerium earths which remain in a single phase extract in close to the theoretical amounts at concentrations up to 5% and even higher.

3. Prepurification of concentrates of the cerium elements should be carried out at high concentrations in the aqueous phase and with small volumes of TBP. Extraction of the cerium earths will be a minimum, and separation of the yttrium earths will be very considerable.

4. It must be admitted that ytterbium and lutecium have a maximum effect on the extraction of the other rare earth elements. The stability of solvates with TBP evidently reaches a maximum with these elements (development of the lanthanide contraction).

5. Extraction of cerium (IV) with tributyl phosphate yields a good product owing to the salting out of all other rare earth elements from the organic phase by the cerium (IV). This is the reason for the equal extraction of Ce (IV) from a solution of one of its salts and from a mixture of rare earth elements.

6. It is possible to wash out the rare earth elements successively from TBP, as was done by Vickery with aqueous solutions by means of Trilon B [6]. Moreover, washing with even a 5% concentration of the yttrium earths or Ce (IV) should free the extract of La, Ce (III), Pr, Nd, and, partially, Sm.

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1-(β-ACETOXYVINYL)-6-METHOXY-3,4-DIHYDRO-
NAPHTHALENE — A NEW BICYCLIC DIENE FOR THE SYNTHESIS
OF STEROID SYSTEMS

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(Presented by Academician B. A. Kazanskii, July 6, 1959)

A series of studies, both in our laboratory [1] and by other investigators [2], has shown that the condensation of 1,2-disubstituted butadienes with unsymmetrical dienophiles yields exclusively, or predominantly, the so-called ordinary isomers of the type of (I) instead of isomers of the type of (II).
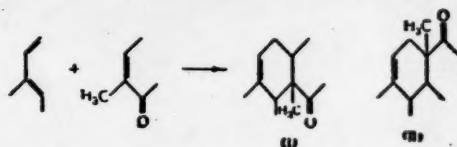
Thus, the diene-condensation route as applied to the synthesis of steroid systems leads only to compounds with functional substituents in the 15 position, instead of the 17 position as in natural substances. In order to modify the diene synthesis so as to obtain products with other structures, it is obviously necessary to introduce some electronegative substituent into the 4 position. Indeed, Winternitz has recently shown [3] that the reaction of 1-(β-acetoxyvinyl)-Δ-cyclohexene (III) with acrylic acid yields the bicyclic acid (IV), which belongs to the class of compounds having a structure of Type (II).
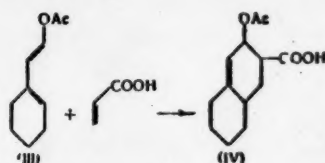
In the present work, we were able to prepare a bicyclic diene of Type (III)*, namely, 1-(β-acetoxyvinyl)-6-methoxy-3,4-dihydronaphthalene (V), and to use it for the synthesis of steroid systems. The starting material was the available 6-methoxytetralone (VI), which was converted to 6-methoxy-1-tetralidenacetaldehyde (VII) by a series of reactions which have previously been described for aliphatic ketones [4]:

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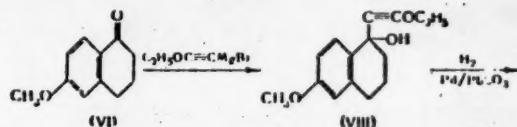
*On original copy, probably should be (II)—Publisher's note.
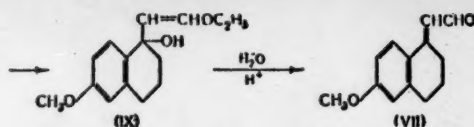
The intermediate acetylenic carbinol (VIII) and the vinylcarbinol (IX) were not isolated. The overall yield of the crystalline aldehyde (VII) was 60%.

Heating aldehyde (VII) with isopropenyl acetate gave 1-(β-acetoxyvinyl)-6-methoxy-3,4-dihydronaphthalene (V), which is the acetate of the enol form of the original aldehyde. This diene proved to be extremely unstable; it formed a tar when distilled under vacuum, and, therefore, it was introduced into reactions without further purification. It should be mentioned that other methods of preparing enols, namely, heating aldehyde (VII) with acetic anhydride in the presence of pyridine (or sodium acetate) and the interaction with a ketone, did not yield the desired results.

Diene (V) reacted with maleic anhydride and with quinone, even at ordinary temperatures, giving adducts (X) and (XI) in yields of 47 and 40% of theoretical, respectively. Hydrogenation of adduct (XI) in the presence of Lindlar's catalyst [5] (palladium on lead carbonate) gave the dihydro compound (XII).
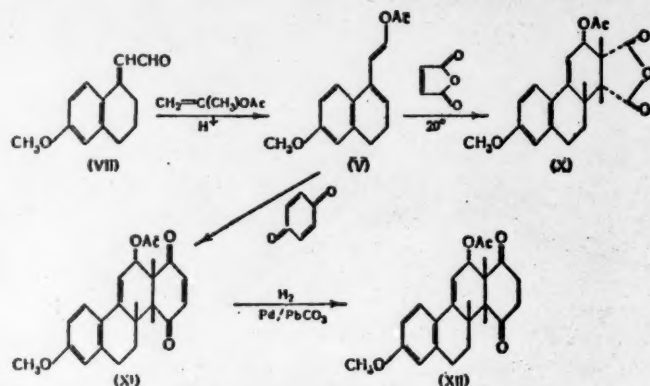
The steric configuration of adducts (X), (XI), and (XII) are proposed on the basis of the principles of retention of configuration of diene and dienophile, on the one hand, and on the basis of the principle of cumulative double bonds, on the other.

Thus, Alder has shown [6] that the condensation of an ester of muconic acid with maleic anhydride leads only to the cis-adduct (XIII).
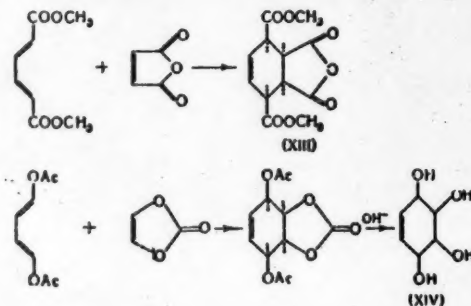
Criegee and Becher [7] synthesized α-conduritol (XIV), the cis configuration of which had previously been demonstrated, by the condensation of 1,4-diacetoxy-1,3-butadiene with vinylene carbonate.

We also carried out the condensation of diene (V) with 2,4-dimethyl-Δ^2-cyclopentene-1,5-dione. This reaction required heating (in benzene), and gave a 35% yield of adduct (XV), which does not contain an acetoxy group.

Apparently, elimination of the elements of acetic acid from the intermediate acetoxy diketone takes place.
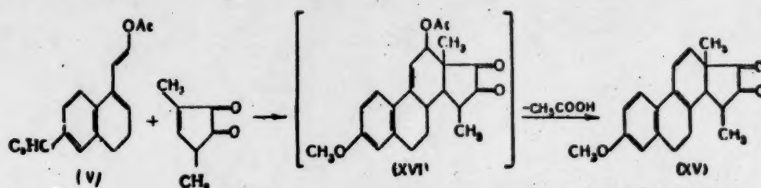
The structure of diketone (XV) will be the subject of future investigations, although the results obtained by Winternitz [3] with diene (III) support the formula given above.

EXPERIMENTAL

Preparation of 6-methoxy-1-tetralidenacetaldehyde (VIII). 2.85 g of freshly distilled ethoxyacetylene [8] in 16 ml of absolute ether was added, with stirring, to a solution of ethylmagnesium bromide obtained from 4.4 g of ethyl bromide, 1 g of magnesium, and 30 ml of absolute ether. At the conclusion of the addition of the ethoxyacetate, the reaction mixture was heated at 35° until ethane was no longer evolved (15 minutes); the reaction mixture was then cooled to 0°, and a solution of 5 g of 6-methoxytetralone in 25 ml of absolute benzene was then added under nitrogen. The mixture was stirred for a half hour at room temperature and 15 minutes at 35°; it was then cooled and decomposed with a cold solution of 1.6 g of ammonium chloride in 100 ml of water. The organic layer was separated, the aqueous layer was washed three times with ether, and the combined extracts were dried with potassium carbonate. Distillation of the solvent under a slight vacuum gave 5.5 g of 1-ethoxyethynyl-1-tetralol (VIII), which was hydrogenated without purification.

5.5 g of this carbinol was dissolved in 25 ml of dry ethyl acetate and hydrogenated in the presence of 1.2 g of Lindlar's catalyst [5] and 0.5 ml of quinoline. Hydrogenation practically ceased after 15 hours, during which time 525 ml of hydrogen (746 mm and 18°) was absorbed; this compares to the theoretically required amount of 505 ml. The catalyst was filtered, 5 ml of 3% H_2SO_4 was added to the filtrate, and the mixture was agitated for 45 minutes. The organic layer was washed with 10 ml of a 5% solution of sodium bicarbonate and dried with magnesium sulfate. The ether was distilled, and the residue was crystallized from ethyl acetate; 3.4 g (60% calculated on the amount of 6-methoxytetralone) of 6-methoxy-1-tetralidenacetaldehyde (VII) was obtained as light yellow crystals with an m. p. of 89-90°, λ_{max} (in heptane) 239, 245 mμ(log ϵ 3.99; 3.91).

$$C_{13}H_{14}O_2. \quad \begin{array}{ll} \text{Found } \%: & \text{C 76.9; 76.8;} \quad \text{H 6.9; 7.05} \\ \text{Calculated } \%: & \text{C 77.2;} \quad\quad\quad \text{H 7.0.} \end{array}$$

The 2,4-dinitrophenylhydrazone was obtained as fine, cherry-colored crystals with an m. p. of 214°: λ_{max} (in heptane) 398 mμ.

$$C_{19}H_{18}O_5N_4. \quad \begin{array}{ll} \text{Found } \%: & \text{C 59.5; 59.7;} \quad \text{H 4.5; 4.8} \\ \text{Calculated } \%: & \text{C 59.7;} \quad\quad\quad \text{H 4.7.} \end{array}$$

Preparation of 1-(β-acetoxyvinyl-3,4-dihydronaphthalene (V). A mixture of 1 g of aldehyde (VII), 5 g of isopropenyl acetate, and fine crystals of p-toluenesulfonic acid was heated for 10 minutes at 120°, during which time about 1 ml of a mixture of acetone and isopropenyl acetate distilled. The cooled mixture was neutralized by agitation with 5 ml of a saturated solution of sodium bicarbonate and extracted with ether, and the extract was dried with sodium sulfate. The ether and isopropenyl acetate were distilled at 30 mm, and 1.1 g of crude diene (V) was obtained; this was used in the diene condensation without further purification.

Condensation of diene (V) with maleic anhydride. 1 g of maleic anhydride was added, under nitrogen, to a solution of 1.1 g of crude diene (V) in 8 ml of absolute benzene, during which there was a slight evolution of

heat, and the mixture was allowed to stand overnight. Distillation of the solvent and crystallization of the residue from toluene gave 0.71 g (47% calculated on the amount of (VII) of the anhydride of 7-methoxy-3α-acetoxy-$\Delta^{4,5,7,13}$ hexahydrophenanthrene-1α, 2α-dicarboxylic acid (X) in the form of white crystals with an m. p. of 127-128°; λ_{max} (in alcohol) 222; 271.5 mμ.

$$C_{19}H_{18}O_6. \quad \begin{array}{ll} \text{Found \%:} & \text{C 66.85; 66.9;} \quad \text{H 5.25; 5.3} \\ \text{Calculated \%:} & \text{C 66.7;} \qquad\qquad \text{H 5.25.} \end{array}$$

Condensation of diene (V) with benzoquinone. 0.3 g of the freshly sublimed quinone was added, under nitrogen, to a solution of 1.1 g of crude diene (V) in 8 ml of benzene; there was a slight evolution of heat. The mixture crystallized after 30 minutes. Recrystallization from benzene gave 0.7 g (40% calculated on the amount of VII) of the acetate of 3-methoxy-$\Delta^{1,3,5,9,16}$-14β-18-nor-D-homoestrapentaene-12α-ol-15,17-dione (XI) in the form of light yellow crystals (which darkened during storage) with an m. p. of 93°; λ_{max} (in alcohol) 269, 277.5 mμ (log ϵ 4.18; 4.18).

$$C_{21}H_{20}O_4. \quad \begin{array}{ll} \text{Found \%:} & \text{C 71.3; 71.3;} \quad \text{H 5.6; 5.65} \\ \text{Calculated \%:} & \text{C 71.6;} \qquad\qquad \text{H 5.7.} \end{array}$$

Hydrogenation of adduct (XI). 150 mg of adduct (XI) in 10 ml of ethyl acetate was hydrogenated in the presence of 100 mg of Lindlar's catalyst. 18 ml of hydrogen was absorbed in 1 hour as compared to the 15 ml required by theory (733 mm, 17°). The catalyst was filtered, the solvent was distilled, and, after crystallization from benzene, there was obtained 100 mg of the acetate of 3-methoxy-$\Delta^{1,3,5,6}$-14β-18-nor-D-homoestratetraene-12α-ol-15,17-dione (XII) with an m. p. of 101-102°; λ_{max} (in alcohol) 268.5 mμ (log ϵ 4.25).

$$C_{21}H_{22}O_4. \quad \begin{array}{ll} \text{Found \%:} & \text{C 71.1; 70.85;} \quad \text{H 6.0; 5.9} \\ \text{Calculated \%:} & \text{C 71.2;} \qquad\qquad \text{H 6.2.} \end{array}$$

A mixture of diketone (XII) with the original adduct (XI) melted at 95°.

Condensation of diene (V) with 2,4-dimethyl-Δ^2-cyclopentene-1,5-dione. A solution of 4.65 g of crude diene (V) and 1.9 g of 2,4-dimethyl-Δ^2-cyclopentene-1,5-dione in 15 ml of absolute benzene was refluxed under nitrogen for 4 hours. The solvent was distilled, 10 ml of ether was added to the residue, and the resulting fine crystals were filtered. 1.9 g of adduct (XII) with an m. p. of 181-182° was obtained. An additional 0.55 g of a material with the same melting point was isolated from the mother liquor. The over-all yield of adduct was 2.45 g (35% calculated on the amount of VII). The pure compound had an m. p. of 183-184° (from alcohol); λ_{max} (in alcohol) 244, 299 mμ (log ϵ 4.60; 4.11).

$$C_{20}H_{20}O_3. \quad \begin{array}{ll} \text{Found \%:} & \text{C 77.6; 77.6;} \quad \text{H 6.5; 6.6} \\ \text{Calculated \%:} & \text{C 77.9;} \qquad\qquad \text{H 6.5.} \end{array}$$

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*Original Russian pagination. See C. B. translation.

A NEW METHOD FOR THE SYNTHESIS
OF α-SUBSTITUTED α-ACYLAMINO ACIDS

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Our investigations of the past few years [1] have resulted in the development of a general method for the introduction of substituents into the alpha position of α-acylamino acids. It was found that oxazolones, which may be obtained from α-acylamino acids, are readily halogenated with the formation of 4-halooxazolones, which are converted by the action of water, alcohols, mercaptans, or amines into the corresponding α-substituted α-acyl-amino acids. The considerable lability of the hydrogen atom in the 4 position of oxazolones suggested that the introduction of substituents into these compounds could be accomplished through derivatives other than the 4-halo derivatives. Thus, a probable route appeared to be acylation of oxazolones with Pb(OAc)$_4$ with subsequent replacement of the acetoxy group by other substituents and simultaneous opening of the oxazolone ring.
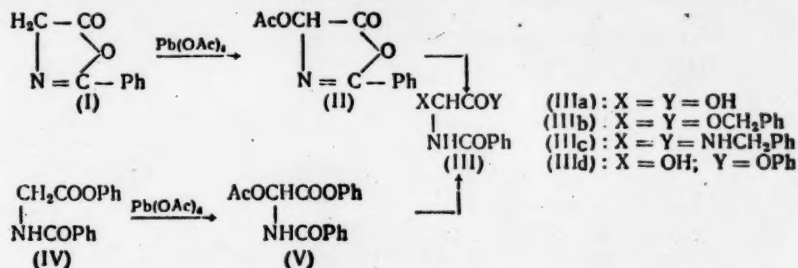
Indeed, it was found that a 5-minute refluxing of a solution of 2-phenyl-5-oxazolone (I) in anhydrous C$_6$H$_6$ gave 4-acetoxy-2-phenyl-5-oxazolone (II), which (without isolation) could be converted by the action of H$_2$O, PhCH$_2$OH (containing HCl), or PhCH$_2$NH$_2$ (in all cases, by stirring for 1-2 hours at 25°) into the corresponding derivatives of α-substituted hippuric acids (IIIa), (IIIb), and (IIIc). These compounds, which were obtained in yields of 25-30%, were identified by means of the substances synthesized by us previously [1] from 4-halo-2-phenyl-5-oxazolone.

Using this method, we were able to introduce an acetoxy group not only into oxazolone (I), but also into the methylene group of the phenyl ester of hippuric acid (IV), which allowed us to avoid azlactonization of the original α-acylamino acid. By refluxing for 6 hours a solution of (IV) in anhydrous toluene with a two-fold excess of Pb(OAc)$_4$, we obtained (after cooling the filtered solution) crystalline phenyl α-acetoxyhippurate (V) in 65% yield. The sturcture of this ester was proved by comparison with a sample prepared by acetylation (refluxing 5 minutes with excess Ac$_2$O [2]) of phenyl α-hydroxyhippurate (IIId) [1]. When the acetoxy ester (V) was refluxed in aqueous dioxane (30 minutes), the acetoxy group was replaced by a hydroxyl group, and the hydroxy ester (IIId) was obtained in 80% yield. Under the conditions described above for the conversion of (II) to (IIIb) and (IIIc), these last two compounds were obtained from (V) in yields of 60 and 80%, respectively. It should be noted that the ease of replacement of the acetoxy group in compounds (II) and (V) has an analogy in the behavior of activated esters [3] and has previously been reported for 4-halomethyl-4-acetoxyoxazolones [4].

Attempts to introduce an acetoxy group into the phenyl esters of N-phtholoyl- and N-carbobenzoxyglycine by the action of Pb(OAc)$_4$ were unsuccessful. This is probably associated with the inability of compounds of this type to undergo tautomerism, $-NH-C(:O)- \rightleftharpoons -N = C(OH)-$, and azlactonization, which increase the reactivity of the α-methylene group.

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DEHYDROGENATION OF CYCLOALKANES WITH FIVE-MEMBERED RINGS OVER PLATINUM CATALYST

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As is well known, studies of the conversion of cycloalkanes containing five- and six-membered rings over catalysts containing metals of Group VIII of the periodic system, platinum in particular, have shown that these two classes of hydrocarbons differ sharply with respect to dehydrogenation. While cycloparaffins containing six-membered rings dehydrogenate smoothly at 300° and ordinary pressures in the presence of platinum or palladium catalysts to the corresponding aromatic hydrocarbons, cyclopentane and its homologs do not undergo dehydrogenation under these conditions, as Zelinskii has shown [1]. More recently, it has been found that, in distinction to cycloparaffins with six-membered rings, pentamethylene hydrocarbons readily undergo ring opening with the formation of aliphatic hydrocarbons at temperatures somewhat exceeding 300° over platinum catalyst in an atmosphere of hydrogen [2]. However, we assumed that these investigations do not exclude the possibility of dehydrogenating the pentamethylene ring under different conditions.
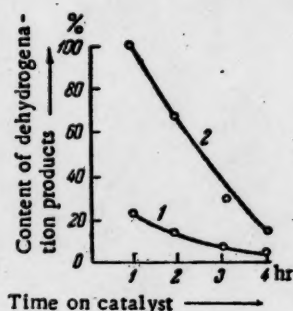
Fig. 1.

The results of the present work show that these hydrocarbons will undergo dehydrogenation at higher temperatures and under reduced pressure. Thus, at temperatures of the order of 550-600° and under reduced pressures as low as 20 mm Hg, cycloalkanes containing five-membered rings are dehydrogenated over Pt-carbon catalyst with the formation of the corresponding cycloalkenes and cycloalkadienes; the extent of conversion to cycloalkadienes is 9-17%. Since the five-membered ring of cycloalkanes does not match the sextet model of the active centers of platinum catalyst, it must be assumed that dehydrogenation of these hydrocarbons over platinum, like dehydrogenation over oxide catalysts, proceeds by an edge mechanism. The fact, established by us, that n-pentane is dehydrogenated in the presence of 5% Pt on carbon at 600° and under reduced pressure confirms, to some extent, the above assumption. n-Pentane is converted to pentenes under these conditions in yields of up to 20%.

The assumption of an edge mechanism for the dehydrogenation of cyclopentane is also in accord with the fact that cyclopentene is found in the reaction products along with cyclopentadiene. In all probability, the dehydrogenation of pentamethylene hydrocarbons takes place in steps, namely: dehydrogenation to the corresponding cycloalkenes takes place first, and the latter then split out hydrogen with the formation of cyclopentadienes.
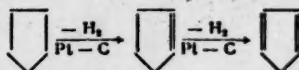
Thus, we are the first to have shown that platinized carbon can, under specific conditions, promote the dehydrogenation of cyclopentane and its homologs to the corresponding cyclopentenes and cyclopentadienes.

EXPERIMENTAL

Cyclopentane (b. p. 49.5° (758), n_D^{20} 1.4070; d_4^{20} 0.7459), methylcyclopentane (b. p. 72° (758), n_D^{20} 1.4100; d_4^{20} 0.7490), and ethylcyclopentane (b. p. 103° (750), n_D^{20} 1.4200; d_4^{20} 0.7670) were contacted with 5% Pt on carbon in a quartz tube at 500-600° and a pressure of 20 mm. The hydrocarbons were charged to the reaction zone in 25-ml portions at a space rate of 0.2 hours^{-1}. At the conclusion of each experiment, the content of cyclopentadiene hydrocarbons in the catalyzate was determined by the method of Afanas'ev [3]; the catalyzate was then subjected to precise fractionation, and the individual fractions were investigated by optical means*. The composition of the gaseous products was determined chromatographically [4]. The results of typical experiments on the dehydrogenation of cyclopentanes are presented in Table 1. As seen from the experimental results presented in Table 1, the dehydrogenation of cyclopentane and its closest homologs proceeds in the presence of platinized carbon with the formation of cyclopentadiene hydrocarbons, and the extent of the conversion to cyclopentadienes increases with an increase in temperature.

TABLE 1

Dehydrogenation of Cycloalkanes Containing Five-Membered Rings in the Presence of 5% Pt on Carbon at a Pressure of 20 mm Hg

Initial hydrocarbon	Expt. temp., °C	Yield of catalyzate, %	n_D^{20} of catalyzate	Yield of cyclopentadienes	
				% of catalyzate	% of hydrocarbon charged
Cyclopentane	500	91.5	1,4100	7	6
	550	85,7	1,4155	10	8
	600	80,6	1,4170	11	9
Cyclopentane in the absence of a catalyst	600	89,9	1,4070	0	0
Methylcyclopentane	550	87,6	1,4150	17	15
	600	80,0	1,4190	20	16
Ethylcyclopentane	550	86,9	1,4330	16	14
	600	81,4	1,4355	19	17
n-Pentane	550	77,2	1,3640	—	—
	600	71,0	1,3670	—	—

The results of the spectroscopic investigations of the catalyzates showed that the cyclopentane catalyzates contained cyclopentene as well as cyclopentadiene. By a detailed investigation of the catalyzates obtained by dehydrogenation of the cyclopentane homologs, it was found that they contained, in addition to the corresponding cyclopentenes and cyclopentadienes, a small amount of demethylation products and also aromatic hydrocarbons in an amount of 5 to 10%. The gaseous products formed by partial decomposition of the pentamethylene hydrocarbons contained methane, hydrogen, and various C_2 to C_4 hydrocarbons.

The spectroscopic determination of the composition of the n-pentane catalyzate obtained in the experiment at 600° showed that it contained 1-pentene (10%) and 2-methyl-1-butene (10%) in addition to unchanged n-pentane (80%). The iodine numbers of the n-pentane catalyzates obtained at 550 and 600° were 48.4 and 72.5, respectively, which correspond to 13 and 20% unsaturated hydrocarbons.

It should be remarked that the activity of Pt-carbon for the dehydrogenation of cyclopentane hydrocarbons gradually decreased from experiment to experiment, as shown in Fig. 1.

Thus, the content of cyclopentadiene hydrocarbons in the methylcyclopentane catalyzate (Fig. 1, Curve 1) was 20% after the first hour, 15% after the second hour, and only 6 and 5% after the third and fourth hours, respectively. At the same time, the activity of the Pt-carbon catalyst for dehydrogenation of cyclohexane was determined after each experiment; after the fourth hour of operation, the activity had decreased from 98 to 16% (Fig. 1, Curve 2). The ability of platinized carbon to promote the dehydrogenation of cyclopentane hydrocarbons was also confirmed by the results of an experiment carried out without a catalyst at 600° and a pressure of 20 mm Hg. In this case, cyclopentane underwent no appreciable change other than partial cracking.

The formation of aromatic hydrocarbons during the dehydrogenation of cyclopentanes may possibly be the result of: 1) isomerization of the alkylcyclopentanes to cyclohexanes with subsequent dehydrogenation to aromatic hydrocarbons and 2) condensation of lower olefins to cyclic systems. The circumstance that aromatic hydrocarbons were formed only during dehydrogenation of alkylcyclopentanes and were practically absent from the dehydrogenation products of cyclopentane could be taken as an indication that the first route is the more probable for the formation of aromatic hydrocarbons.

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THE SOLUBILITY OF TRANSITION METAL COMPOUNDS
IN THE LIGHT OF CRYSTAL FIELD THEORY

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(Presented by Academician A. A. Grinberg, July 1, 1959)

If a metal ion with an incomplete shell of electrons comes into a field of anions or polar molecules, the ground state is split into energy sublevels, the number of which can be calculated by group theory [1] (intramolecular Stark effect). Filling the sublevels lower than the ground state of the gaseous ion with electrons leads to a gain in energy, i. e., to the appearance of the so-called extra stabilization energy. The amount of extra stabilization energy can be calculated according to the formula [2, 3]

$$E = \rho V, \tag{1}$$

where V is the difference between two energy levels, and ρ is a coefficient which depends on the electronic structure of the metal ion and on the spatial distribution of the anions or molecules creating the field around the metal ion.

The process of solution of a salt in water is expressed by the equation:

$$MX_{m(s)} + nH_2O + aq = M(H_2O)_{naq}^{z+} + X_{aq}^{n-}. \tag{2}$$
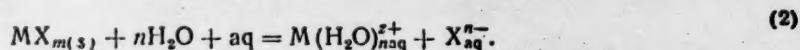
It is apparent from this equation that during solution, the field created by anions X in the crystal changes to a field created by H_2O molecules which form part of the aquo ion. The effect of the crystal field during this substitution is manifested as the difference in the extra stabilization energy*:

$$\Delta E = \Delta\rho V_{H_2O} + \rho_X \Delta V; \tag{3}$$

where the subscript X refers to the anion of the salt and H_2O refers to water molecules. Modification of Equation (3) leads to the expression:

$$\Delta E = \Delta_f V_{H_2O} + \rho_X \Delta V, \tag{4}$$

where

$$\Delta\rho = \rho_{H_2O} - \rho_X, \qquad \Delta V = V_{H_2O} - V_X.$$

If it is assumed that the aquo ion has the composition $M(H_2O)_6^{n+}$ and an octahedral structure [4] and that in crystals of the salt MX_n there are various deviations from cubic symmetry, it becomes possible, though only to a first approximation, to plot the general course of the changes in values of ΔE. Table 1 presents the results of such calculations for various ratios of V_{H_2O} to V_X. Values of the coefficient ρ_X for a tetragonal field were assumed [2]; they should be approximately the same for a field with hexagonal symmetry.

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* Positive values of ΔE denote that process (2) is exothermic, and vice versa.

TABLE 1

Values of ΔE Calculated by Equation (4)

Ion	I $V_{H_2O} = V_X$	II $V_X/V_{H_2O} = 1.5$	III $V_X/V_{H_2O} = 2$	IV $V_X/V_{H_2O} = 2.5$
Mn^{2+}	0	0	0	0
Fe^{2+}	1	0.5	0	-0.5
Co^{2+}	2	1.0	0	-1.0
Ni^{2+}	3	1.5	0	-1.5
Cu^{2+}	-4	-3.0	-5.0	-7.0
Zn^{2+}	0	0	0	0

The values presented in Table 1 show that the change in the heat of solution of the salts under consideration with atomic number is nonlinear. As an example, consider the heats of solution of the salts in the series MnX_m, FeX_m, NiX_m, CuX_m, and ZnX_m. If the values corresponding to the manganese and zinc salts are connected by a straight line (when atomic number is plotted along the abscissa), the copper salts always deviate in an exothermic direction (negative values of ΔE). The sign and value of the deviations of the remaining salts depend on the strength of the field (V_X); the deviation is toward an endothermic process when the field is strong.

Table 2 presents literature values [5] of the heats of solution of the halides, hydroxides, sulfates, and sulfides of the metals under consideration and deviations of these values from those found by linear interpolation. For convenience in making comparisons, the sign of the deviations has been reversed. In the case of the halides, the course of the change in heat of solution suggests a change of the first type $\Delta E (V_{H_2O} \leq V_X)$, in the case of the hydroxides and sulfates, the change would seem to be of the second or third type $E(V_X > V_{H_2O})$, while in the case of the sulfides, the change appears to be one of the fourth type $(V_X > V_{H_2O})$.

TABLE 2

Heat of Solution, ΔH, and ΔE in kcal./mole for Certain Compounds

Type of compound	ΔH						ΔE			
	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
MCl_2	-16.7	-19.4	-18.3	-19.6	-12.2	-17.1	2.6	1.5	2.7	-4.8
MBr_2	-19.4	-19.1	-18.4	-18.9	-8.8	-16.0	0.4	0.4	1.5	-7.9
MI_2	-19.7	-19.0	-21.5	-21.5	-6.2	-13.2	0.6	1.3	5.7	-8.3
$M(OH)_2$	3.6	4.9	5.2	4.6	1.7	7.2	-0.6	-0.2	1.1	-6.2
MSO_4	-15.0	-15.5	—	-15.1	17.5	19.4	-0.4	—	-2.6	-1.1
MS	5.3	11.7	15.3	15.4	37.0	21.1	-3.3	-3.7	-0.7	-19.1

TABLE

Solubilities of Certain Compounds (log s. p.) and Deviations from a Linear Dependence, ΔE [6, 7]

Type of compound	-log s. p.						ΔE'			
	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
$M(OH)_2$	14.15	15.02	15.7	14.87	19.88	16.7	-0.3	-0.5	0.8	-3.7
MOx_2 [6]	17.80	—	21.60	22.75	28.30	25.49	—	-0.6	-0.2	-4.3
MS [7]	14.96	19.4	22.5	23.8	37.5	26.1	-2.2	-3.1	-2.2	-13.7

* Ox—hydroxyquinolate.

The solubility of salts is characterized by the solubility product (s. p.). The logarithm of the s. p. is proportional (at constant temperature) to the negative of the change in free energy.

$$\Delta Z = -2.3 \, RT \lg \text{ s. p.} \tag{5}$$

If it be assumed that for the series of salts being considered, the entropy change in Reaction (2) is approximately constant, it is understandable that log s. p. varies directly with ΔH.

The logarithms of the solubility products for the hydroxides, hydroxyquinolates, and sulfides of the series of metals under consideration and their deviations from linearity are presented in Table 3. These data are in good agreement with the data presented in Tables 1 and 2.

Thus, this collection of the available experimental data confirms the rule derived from theoretical considerations: the solubility of transition metal compounds (in particular, compounds of manganese, iron, cobalt, nickel, copper, and zinc) does not vary linearly with atomic number, the solubility of copper salts (and, in general, of ions of types d^4 and d^9) always deviates on the side of decreased solubility, and the logarithms of the solubility products of the remaining salts deviate from linearity either positively (in the case of weak crystal fields) or negatively (in the case of strong fields).

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ON THE INTERACTION OF SUBGROUP VIIA ELEMENTS
WITH TRANSITION METALS

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The study of the elements of Subgroup VIIA (Mn, Tc, Re) is of great interest from the point of view of the theory of the transition metals. It is known that Mn is an anomalous metal with respect to the nature of the bonding forces between atoms, with respect to crystal structure, and with respect to a number of physical properties. The structure of its α- and β-modifications is more characteristic of metallic compounds than of pure metals.

TABLE 1

Some Physical Properties of the Elements of Subgroup VIIA of the Periodic System of D. I. Mendeleev

Element	Atomic No.	Atomic wt.	Atomic radius	M.p., °C	B.p., °C	Modification	Type of space lattice	Parameter, kX	Spec. Elec. Res., ohm-cm · 10⁻⁸
Manganese						α to 727°	Complex body-centered cubic. 58 atoms per unit cell	$a = 8,894$	150—260
						β 727 to 1090°	Same, 20 atoms per unit cell	$a = 6,300$	90
	25	54,93	1,30	1244	2150	γ 1090 to 1130°	Face-centered cubic	$a = 3,854$	40
						δ 1130 to 1244°	Body-centered cubic	$a = 3,074$	—
Technetium	43	99	1,36	2700	—	—	Close-packed hexagonal	$a = 2,729$ $c = 4,379$ $c/a = 1,604$	—
Rhenium	75	186,31	1,37	3170	5870	—	Close-packed hexagonal	$a = 2,7553$ $c = 4,4493$ $c/a = 1,6143$	21,1

Element	Modification	Temp. coeff. elec. res. × 10⁻⁴	Density, g/cc	Hardness, kg/sq. mm at 20°	Heat capacity, cal./°/mole	Coeff. linear expansion × 10⁻⁶ at 20°	Modulus of elasticity, kg/sq. mm	Spec. Mag. Suscep. × 10⁻⁶	Compressibility × 10⁻⁶ sq. cm./kg
Manganese	α	2—3	7,44	950—1000	0,114	22,3	20160	9,6	0,84
	β	12	7,29	990	0,155	24,9			
	γ	60	7,24	100—150	0,120	14,8			
Technetium			11,5	—	—	—	—	—	
Rhenium		31,1	20,9— 21,40	250	0,0322	12,45 (001) 4,67 (100)	47000	0,369	

Indeed, in a number of transition metal systems there are compounds having a structure isomorphous with these modifications [1; 2]. A characteristic feature of rhenium is its active interaction with elements of Subgroups IVA, VA, and VIA with the formation of σ and χ -phases in binary systems [3, 4]. Manganese and rhenium are analogs with respect to the formation of chemical compounds (oxides, acids, etc.); however, up to the present there has been no work to determine whether this analogy extends to the interaction of these elements with metals.

The data of Table 1 show the sharp differences in the physical properties of Mn and Re, particularly with respect to melting point, electrical resistance, and paramagnetic susceptibility, but also with respect to crystallochemical characteristics. Technetium, a radioactive element prepared synthetically in a nuclear reactor and an element which still has not been very well studied, is apparently closely similar to rhenium in its properties, and it does have the same crystal structure. Tc and Re are superconductors, while Mn is not.

A consideration of the properties of Re and Mn plus the available information relative to interactions between these metals does not permit one to form any conclusion as to the existence of analogies between them. Indeed, in all systems of transition metals belonging to the same group of the periodic system of D. I. Mendeleev, systems such as Ti−Zr, Mo−W, Ni−Pt, etc., no compounds are formed other than ordered solid solutions of the

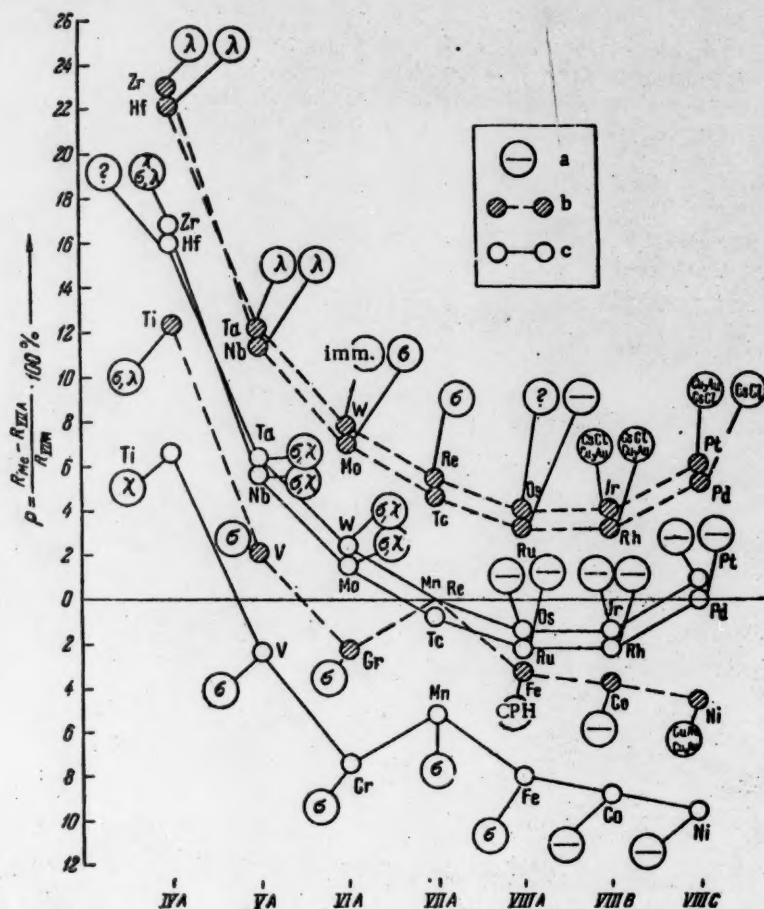Fig. 1. Dependence of the size factor of transition metals (b−with respect to manganese and c−with respect to rhenium) on the number of the subgroup of the periodic system of D. I. Mendeleev; a−Intermetallic compounds are not formed in the system; χ−a χ-phase is formed in the system; λ−a Laves phase is formed in the system; σ−a σ-phase is formed in the system; CsCl−a phase of the CsCl type is formed in the system.

type of CuAu and Cu$_3$Au. At the same time, a σ-phase exists in the Re−Mn system [5], which indicates a stronger chemical interaction between the components, an interaction previously known only for elements of different groups. A more detailed analysis of the interaction of manganese and rhenium with transition metals reveals a marked similarity between these elements with respect to the formation of metallic phases. Figure 1 shows the dependence of the size factor P (with respect to Mn and Re) on the number of the group of the periodic system for all of the transition metals.

The calculations were carried out by means of the equation $P = \dfrac{R_{Me} - R_{VII}}{R_{VII}} \cdot 100\%$, where R_{Me} is the atomic radius of a given transition metal and R_{VII} is the atomic radius of Mn (or Re). The values of the atomic radii were taken from [6].

Those compounds which are formed in binary systems of Mn or Re with the corresponding transition metals are indicated in Fig. 1. In binary systems with Subgroup IVA and VA elements having size factors greater than + 10%, both Mn and Re form Laves phases having structures of the type of MgZn$_2$ and MgNi$_2$ (ZrRe$_2$, ZrMn$_2$, TiMn$_2$, TaMn$_2$, and NbMn$_2$). All of these compounds are formed from the liquid and are stable down to room temperature.

It should be remarked that in only two cases is there observed the existence in one system of Laves phase and other compounds (Zr−Re and Ti−Mn); i. e., with a favorable ratio of the atomic radii of the components, the Laves phase is the more stable phase, and the formation of other phases is suppressed. A sigma phase is observed in 14 Mn and Re binary systems, which indicates a special tendency of Subgroup VIIA elements toward the formation of compounds of this type. The value of the size factor for corresponding binary systems varies within wide limits (see Fig. 1). It is characteristic that Mn and Re form binary compounds of the type of Laves phases or σ-phases with all of the transition metals to the left of Group VII of the periodic system of elements of D. I. Mendeleev •[7].

It is reported in reference [4] that Re forms a χ-phase (α-Mn structural type) in binary systems with metals of Subgroup IVA, VA, and VIA under conditions such that P > 0. In the case of Mn binary systems, the structure analogous to a χ-phase is a solid solution based on α-Mn. On the basis of considerations discussed in reference [4], it might be assumed that the elements with the most favorable size factor (V, Mo, Re) should be more soluble in α-Mn. The interaction of Re and Mn with elements of Group VIII is different. As a rule, in binary systems with these elements, phases with a complex crystal structure are not formed. Rhenium, for example, forms a compound only with Fe, and with Co and Os it forms a continuous series of solid solutions. Manganese forms a continuous series of solid solutions with a face-centered cubic lattice(γ-Mn)with elements of the first long period (Fe, Co, Ni). Only a metastable phase with a close-packed hexagonal structure is known in the Fe−Mn system. Ordered phases having a structure of the type of CuAu and Cu$_3$Au have been noted in the Mn−Ni system. Broad regions of compounds with a structure of the type of CsCl exist in the systems Mn−Rh, Mn−Pd, Mn−Ir, and M$_n$−P$_t$ in the neighborhood of equimolar composition. Moreover, ordered phases with a structure of the type of Cu$_3$Au are known in systems of Mn with Ir, Rh, and Pt. The fact that Re and Mn can form continuous series of solid solutions or simple diagrams of the eutectic (peritectic) type just with Group VIII elements shows that both of these elements by nature approach the metals of Group VIII of the periodic system.

All of the material presented above suggests the conclusion that an extensive analogy exists between Mn and Re in the formation of alloys with transition metals. This is indicated first by the character of the interaction of these metals with the elements to the right and to the left of Group VII of the periodic system: with the metals of Subgroups IVA, VA, and VIA, compounds are formed; with the metals of Group VIII, solid solutions with simple structures or compounds with a simple structure are formed. Mn and Re form the same types of phases in binary systems with the metals of the titanium, vanadium, and chromium groups. Both of these elements have special tendencies toward the formation of σ-phases. The structure corresponding to the low-temperature modification of Mn arises in Re systems as an independent compound. Unfortunately, up to the present it has been impossible to form a complete classification of binary systems based on the elements of Subgroup VIIA in view of the absence of work on technetium alloys. On the basis of the above considerations, it is only possible to assume that the behavior of Tc in alloys should be similar to the behavior of Re. In particular, according to Fig. 1, Tc would be expected to form χ-phases in alloys with Ti, Nb, and Ta, σ-phases in alloys with Cr, Mo, and W, and Laves phases in alloys with Zr and Hf. It would be extremely interesting to determine whether the formation of σ-phases is possible in Tc−Mn and Tc−Re alloys.

• An exception is the system Mn−W owing to immiscibility in the liquid and solid states. The Re−Hf system has not been studied.

The relatively clear classification of the binary systems of transition metals with Mn and Re and also the limited collection of phases observed in these systems are associated with the key position of Subgroup VIIA among the transition metals.

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INVESTIGATION OF THE STRUCTURE OF In_2Bi and InBi ALLOYS

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Two intermetallic compounds exist in the In−Bi system: In_2Bi and InBi. The first of them, In_2Bi, crystallizes in hexagonal syngony (AlB_2 type structure, Federov group C6/mmm), while the second, InBi, crystallizes in tetragonal syngony (PbO type structure, Federov group P4/nmm).

It appeared to be of interest to investigate the structure of the liquid alloys from two directions: 1) to trace the change in the structure of the melt associated with a change in the structure of the solid alloy, and 2) to determine the effect of temperature on the structure of the intermetallic compound in the liquid state.

With this aim, the structure of In_2Bi_{liq} at 90, 110, and 200° C and the structure of $InBi_{liq}$ at 110° were studied. The electron diffraction method used to investigate the structure has been described previously [1].

The normalized intensity curves obtained in the investigation are shown in Fig. 1. The following should be noted here: An increase in the temperature led to a decrease in the maxima toward lower values of S (thus, the position of the first maximum on the normalized intensity curve for In_2Bi_{liq} changed from 2.17 S units at 90° to 2.09 S units at 200°; there was also a decrease in the sharpness of the maxima on the intensity curves (in place of the third maximum, there was an inflection in the normalized intensity curve for In_2Bi). No additional maxima were observed on changing from In_2Bi to InBi, though there was an insignificant shift in the positions of the maxima in the direction of lower angles. Radial distribution curves were calculated on the basis of the normalized intensity curves (Fig. 2). The positions of the individual maxima on the radial distribution curves are given in Table 1.

TABLE 1

Temp. °C	Compound	Position of maximum, r, A			Area of first maximum	Coordination number
		1	2	3		
90	In_2Bi	3,32	4,63	5,69	10,4	Bi—In 10,1 / In—Bi 5,0
110	In_2Bi	3,35	4,70	5,73	9,35	Bi—In 9,1 / In—Bi 4,6
200	In_2Bi	3,57	4,72	—	9,28	Bi—In 9,0 / In—Bi 4,4
110	InBi	3,42	4,60	6,00	13,08	Bi—In 8,36 / In—Bi 8,36

By comparing the radial distribution curves obtained at the different temperatures, it is possible to trace the disappearance of the first coordination sphere. With an increase in the temperature, the intensity of the first maximum decreased (the height decreased from 18.39 at 90° to 14.50 at 200°); the maximum became more sloping and shifted in the direction of higher values of $\underline{r}$.
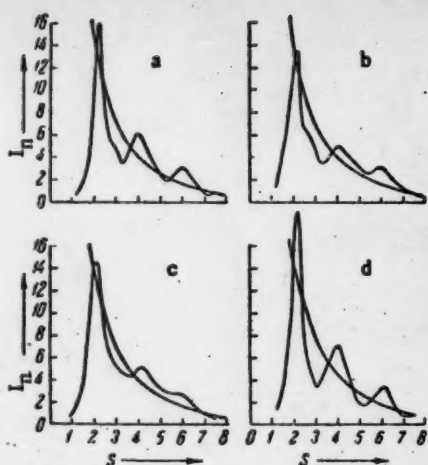
Fig. 1. Normalized intensity curves for liquid In$_2$Bi (a—at 90°, b—at 110°, c—at 200°) and InBi (d—at 110°).
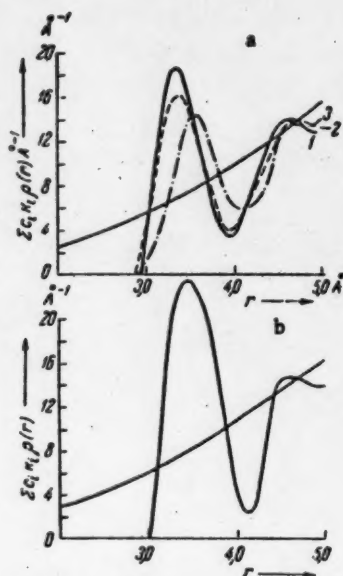
Fig. 2. Radial distribution curves.
a—for In$_2$Bi (1—90°, 2—110°, 3—200°),
b—for InBi (110°).

If it is assumed that each atom is surrounded chiefly by atoms of the other kind, i. e., that the nearest neighbors in the melt are approximately the same as those in the solid state, the coordination number can be calculated by means of the formula:

$$n_{ij} = \frac{S_{max}}{2c_i \cdot k_i \cdot k_j} \cdot \qquad (1)$$

The results of the calculations are presented in Table 1.

In solid In$_2$Bi, each In atom is surrounded by 6 Bi atoms, and each bismuth atom is surrounded by 12 In atoms. Upon comparing these data with the data presented in Table 1, it can be said that our assumption as to the nature of the closest neighbors in In$_2$Bi melts is basically justified—the coordination number in the liquid is close to that in the solid state. With an increase in temperature, there is a change in the coordination number owing both to a change in the packing density and to the introduction of the other kind of atoms into the coordination sphere. Table 1 presents coordination numbers for liquid In$_2$Bi at high temperatures; these were calculated with the assumption that the closest neighbors remain unchanged.

However, another assumption is possible; a statistical distribution of the different atoms in the melt can be assumed. With this assumption, the calculated average coordination number is 6.7; it is close to the coordination number of pure indium and bismuth, but it is very low as compared to the coordination number in the solid state.

With a change from In$_2$Bi to InBi, the coordination number changes from 12 and 8 for bismuth and indium, respectively, to 8 and 8. Calculations by formula (1) showed that in InBi$_{liq}$ at 110°, each indium atom is surrounded by 8.3 atoms of bismuth and each bismuth atom by 8.3 atoms of indium.

It is clearly evident on the basis of the present data that there is a definite correspondence between the structure of the alloys and the structures of the corresponding solid phases of the stoichiometric compounds.

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THE MECHANISM OF CARBON FORMATION DURING DEHYDRATION
OF ISOPROPYL ALCOHOL OVER COPPER – SILICA GEL CATALYST

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The formation of tarry and carbonaceous substances which cover the surface of the catalyst has been observed in all kinds of organic reactions occurring through heterogeneous catalysis. It may be assumed that the concept of tar- and carbon-formation processes as polycondensation reactions of the original organic substances or of certain products of their preliminary conversion has already been confirmed [1-9]. There are now only a few who adhere to the old ideas of Berthelot [10], according to which the carbon is "free carbon" formed as a result of the complete decomposition of the organic substance to the elements.
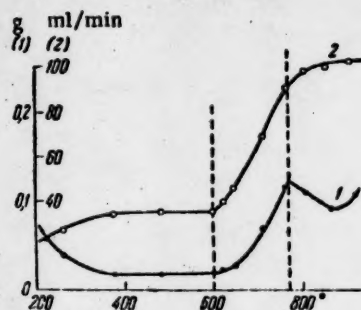
Fig. 1. Change in the rate of carbon formation (1) and in the rate of evolution of gaseous products (2) with an increase in temperature during the decomposition of isopropyl alcohol. (Contact time, 6 seconds).

Our work, in which we studied tar and carbon formation during the decomposition of ethyl alcohol and hydrocarbons over catalysts [11], has shown that there are several mechanisms of carbon formation, and that one which operates in a given case depends on the temperature conditions and on the nature of the simplest preliminary conversions undergone by the original substance. Thus, in the case of ethyl alcohol at 200-600°, the carbon is formed by a low-temperature mechanism which proceeds through the polycondensation of acetaldehyde. At 750-950°, the carbon is formed by a high-temperature mechanism through polycondensation of the simplest paraffinic and aromatic hydrocarbons, which are the products of the decomposition of the alcohol, and also through the direct polycondensation of the original alcohol.

The present work investigating tar and carbon formation during the decomposition of isopropyl alcohol in the temperature range of 200-950° over copper—silica gel catalyst showed that, as in the case of ethyl alcohol, there are several mechanisms of carbon formation (Fig. 1): a low-temperature mechanism operating at 200-600° (polycondensation of acetone), a high-temperature mechanism operating at 775-950° (dehydrocondensation of saturated and aromatic hydrocarbons resulting from the decomposition of the alcohol and polycondensation of the original alcohol itself), and, in contrast to ethyl alcohol, a third, "intermediate" mechanism operating at 600-775°, which operates through polycondensation of the propylene resulting from the dehydration of the alcohol. In the work, major attention was given to a consideration of the features of the intermediate mechanism of carbon formation during dehydration of isopropyl alcohol.

The work was carried out at atmospheric pressure in a flow system used for investigations of heterogeneous catalysis; the quartz reactor was of a type which could be readily removed, so that the amount of carbonaceous material formed could be determined gravimetrically [12]. The experimental method was similar to that used previously [6]. A fresh portion of catalyst, 4 ml, was used for each experiment. The catalyst contained 0.0002 mole of copper per grain, and was prepared by impregnation of KSM silica gel with a solution of copper nitrate
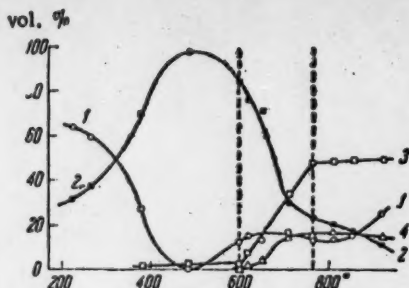
Fig. 2. Change in the composition of the gaseous products formed during decomposition of isopropyl alcohol at various temperatures. (Contact time, 6 seconds). Components of the gas: 1—Hydrogen, 2—olefins, 3—saturated hydrocarbons, 4—carbon monoxide.

Fig. 3. Composition of the hydrocarbon part of the gaseous products of the decomposition of isopropyl alcohol in the regions of intermediate and high-temperature mechanisms. (Contact time, 6 seconds). Components of the gas: 1—Methane, 2—ethane, 3—ethylene, 4—propane, 5—propylene.

and subsequently drying, calcining, and reduction in situ. The time of each experiment was 1 hour. The isopropyl alcohol had the following constants: b. p. 82° (758 mm Hg); n_D^{20} 1.3774; d_4^{20} 0.7856. The rate of evolution of gaseous products, measured at STP, was recorded by means of an UGSP automatic gas meter. The liquid, tarry, and gaseous alcohol-decomposition products were collected and analyzed. Analysis of the gases was carried out by means of a VTI gas analyzer and a gas chromatography apparatus. Ultraviolet absorption spectra of the tar were taken with an SF-4 spectrophotometer.

If one compares the changes in the rate of carbon formation and the rate of evolution of gaseous decomposition products (Fig. 1) with the changes in the composition of the gaseous products (Figs. 2 and 3) occurring with an increase in temperature, it can be seen that there is a parallel among the increase in the rate of carbon formation by the intermediate mechanism, the increase in the rate of evolution of gaseous decomposition products, and the increase in the rate of methane formation. A sharp increase in all of these values began at 600°, where the intermediate mechanism of carbon formation begins to be effective, and ceased at 775°, where the intermediate mechanism begins to be replaced by the high-temperature mechanism. The concentration of methane in the gases formed below 600° was close to zero, it reached 50% at about 775°, and remained at this level with further increases in temperature, when the high-temperature mechanism came into play. The concentration of hydrogen remained practically constant (15-18%) over the entire temperature range of the intermediate and high-temperature mechanisms of carbon formation (600-950°).

Similar results were obtained during the investigation of the effect of contact time on the rate of carbon formation and on the composition of the products formed during the decomposition of isopropyl alcohol at 730° (Fig. 4). With an increase in contact time over the range 3-12 seconds, the rate of carbon formation increased, and it reached a certain constant value at the higher contact time. The rate of methane formation underwent precisely the same changes; its course was in every way similar to the course of the rate of carbon formation. Totally different changes were observed for the rates of formation of other products; the rate of H_2 formation remained practically constant at all values of the contact time.

Thus, there exists a direct connection between the rates of formation of carbonaceous material and methane, and there is no such connection between the rate of carbon formation and the rate of evolution of hydrogen. The following are features of the polycondensation of propylene: splitting out of methane proportionally to the consumption of propylene and the nonexistent role of dehydrogenation; these suggest that the intermediate mechanism of carbon formation during the dehydration of isopropyl alcohol at 600-775° may be represented by the following scheme:

$$\begin{array}{c} H_3C \\ H_3C \end{array}\!\!\diagdown\!\!CH\text{-}OH \xrightarrow[\substack{\text{Catalytic} \\ \text{dehydration}}]{Cu-SiO_2} H_3C-CH=CH_2 + H_2O$$

etc.

The mechanism could be continued in a similar manner down to the formation of pyrene, coronene, and complex carboid nuclei.

According to this scheme, alternation of the following three elemental stages may be noted in the polycondensation of propylene to carbon: condensation of the original propylene, cyclization, and demethanation. The process can be accompanied by the side reactions of exhaustive demethanation of the trimethylcyclohexane, which leads to benzene, and the exhaustive demethanation and dehydrogenation of other hydroaromatic hydrocarbons, which leads to naphthalene, phenanthrene, and other polynuclear aromatic hydrocarbons. Naphthalene, biphenyl, phenanthrene, triphenylene, perylene, coronene, dibenzopyrene, and others were actually detected by u. v. spectroscopy in the tarry polycondensation products. Naphthalene, biphenyl, and phenanthrene were also isolated in the pure state by fractional crystallization, and were identified by melting point.

The general scheme presented for the polycondensation of propylene can have several variants during its actual operation. For example, side reactions leading to aromatic compounds can take place to various degrees as compared to the main course of the reaction. Depending on these side reactions, the highly condensed tarry and carbonaceous carboid hydrocarbons, to which development of the scheme logically leads, can, in extreme cases, be either aromatic or hydroaromatic systems, and in the intermediate case, they can be a mixture of the one with the other. This was confirmed by the results of the analyses (in %) of the coked catalysts. 1-Hour experiment at 765°: C, 1.89 and 2.08; H, 0.16 and 0.34; composition $(C_{17}H_{25})_x$: 6-hour experiment at 730°; C, 421 and 4.29; H, 0.11 and 0.18; composition $(C_5H_2)_x$. In the first case, the composition of the carbonaceous material corresponds to a methylated 12- to 15-ring hydroaromatic system obtained after 12-15 cycles according to the left-hand part of the scheme; in the second case, the composition corresponds to a 12- to 15-ring aromatic system formed in accordance with the right-hand part of the scheme.
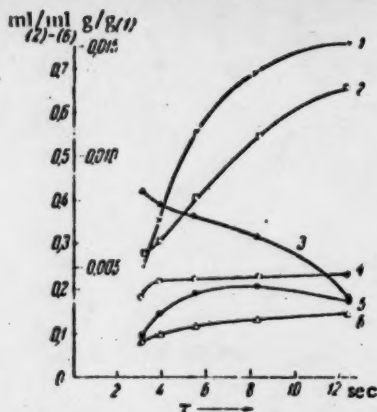
Fig. 4. Change in the composition of the decomposition products of iso-propyl alcohol and in the rate of their formation with a change in contact time; temperature, 730°, which is in the region of the intermediate mech-anism of carbon formation. Decom-position products: 1—Carbonaceous material, 2—methane, 3—propylene, 4—hydrogen, 5—ethylene, 6—carbon monoxide.

Other variations in the scheme are possible; these could be expressed as a different alternation of the removal of meth-yl groups of the intermediate hydroaromatic hydrocarbons, as changes in the order of alternation of the stages in the poly-condensation cycles, etc., and they are also capable of exert-ing an effect on the structure of the polycondensation products. It was due to precisely this existence of side processes that we actually found anthracene, biphenyl, triphenylene, and other products in addition to naphthalene and phenanthrene; these products could be obtained only by the indicated variations of the scheme presented above. However, in all variants, the same elemental reactions occur during the process: condensa-tion of propylene, cyclization, and demethanation, which com-prise separate stages in each of the numerous repetitions of the polycondensation cycles.

It is evident that the "intermediate" mechanism of car-bon formation in the case of n-propyl alcohol will be the same.

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ORGANOPHOSPHORUS DERIVATIVES OF ETHYLENIMINE. DIETHYLENAMIDES OF PHOSPHORUS ACIDS

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(Presented by Academician B. A. Arbuzov, July 6, 1959)

The first compound of this type was synthesized by H. Bestian, who described the synthesis of the diethylenamide of ethylphosphoric acid [1].

The synthesis of a number of ethylenamides of various phosphorus acids (phosphoric, phosphorous, thiophosphoric, and ethylthiophosphoric) is described in the present communication.

TABLE 1

Diethylenamides of phosphorus acids

Formula of compound	B. p., °C/mm	d_4^{20}	n_D^{20}	MR found	MR calc.	P, % found	P, % calc.	Yield, % of theoretical
$C_2H_5OP\left[N{<}^{CH_2}_{CH_2}\right]_2$	76—77/11	1,0444	1,4810	43,59	43,03	19,27 19,59	19,37	70
$C_2H_5OP\left[N{<}^{CH_2}_{CH_2}\right]_2$ ‖O	91—92,5/2	1,1688	1,4712	42,16	41,91	17,60 17,99	17,62	70
$nC_3H_7O\left[PN{<}^{CH_2}_{CH_2}\right]_2$ ‖O	103,5—104/1,0	1,1263	1,4681	46,90	46,53	16,06 16,16	16,31	60
$nC_4H_9P\left[N{<}^{CH_2}_{CH_2}\right]_2$ ‖O	105–106/0,5	1,1008	1,4676	51,38	51,15	15,05 15,17	15,20	80
$C_2H_5OP\left[N{<}^{CH_2}_{CH_2}\right]_2$ ‖S	90—91/0,2	1,1663	1,5198	49,25	49,40	16,14 16,37	16,14	80
$n\text{-}C_3H_7OP\left[N{<}^{CH_2}_{CH_2}\right]_2$ ‖S	103,5—104,5/0,4	1,1300	1,5129	54,41	54,02	15,22 14,94	15,05	80
$n\text{-}C_3H_7OP\left[N{<}^{CH_2}_{CH_2}\right]_2$ ‖S	79–80/0,1	1,1237	1,5098	54,81	54,02	15,12 15,24	15,05	68
$n\text{-}C_4H_9OP\left[N{<}^{CH_2}_{CH_2}\right]_2$ ‖S	113,5–114,5/0,2	1,1666	1,5087	59,32	58,64	13,94 14,24	14,09	74
$C_2H_5P\left[N{<}^{CH_2}_{CH_2}\right]_2$ ‖S	89/0,5	1,1267	1,5402	49,04	48,27	17,57	17,62	55

The properties of the diethylenamides prepared in the present work were similar to the properties of the monoethylenamides of phosphorus acids described by us previously [2, 3, 4]. Thus, for example, diethylamine opens the ethylenimine ring with the formation of the corresponding organophosphorus derivatives of ethylenediamine

$$C_2H_5OP \begin{bmatrix} N \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \end{bmatrix}_2 + 2HN(C_2H_5)_2 \rightarrow C_2H_5OP[NH-CH_2-CH_2N(C_2H_5)_2]_2$$
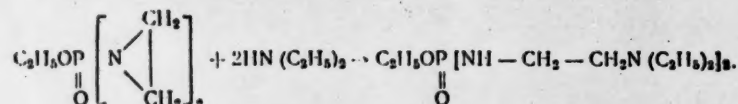
Diethylenamides of phosphorus acids are potential cytostatic (antitumor) agents, and from this point of view, they require close study.

The di- and triethylenamides of phosphorus acids previously investigated in this regard do have cytostatic properties [5-8].

The compounds were of the following types:

$$(C_2H_5)_2NP \begin{bmatrix} N \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \end{bmatrix}_2$$

$$O=P \begin{bmatrix} N \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \end{bmatrix}_3 \qquad S=P \begin{bmatrix} N \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \end{bmatrix}_3$$
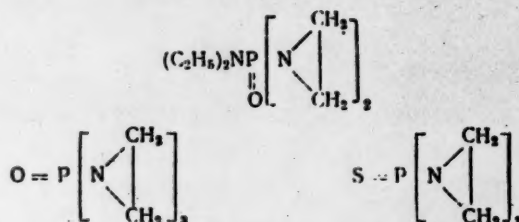
A paper has comparatively recently been published by Kropacheva and Parshina [9], who synthesized a series of ethylenamides of phosphoric acid having the general formulas:

$$Ar NHP \begin{bmatrix} N \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \end{bmatrix}_2 \qquad Ar OP \begin{bmatrix} N \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \end{bmatrix}_2$$
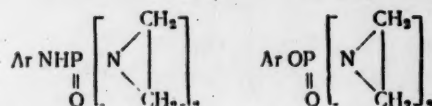
Preliminary data on the biological properties of the compounds prepared by them were published in 1956 [10]. A still earlier article [11], was published by Kornev and Protsenko on the synthesis of diethylenamides of phosphoric acid of the form:

$$ArNHP \begin{bmatrix} N \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \end{bmatrix}_2$$
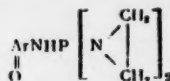
Kropacheva and Parshina made no mention either of this article or of two recent articles of ours [2, 3].

The literature also contains several patents which indicate that organophosphorus derivatives of ethylenimine have therapeutic value [12].

The formulas and constants of the substances prepared by us are presented in Table 1.

EXPERIMENTAL

All of the phosphorus acid diethylenamides described in this communication were prepared by the method used for the synthesis of the similar monoethylenamides [1, 2].

The addition of diethylamine to the diethylenamide of ethylphosphoric acid: 10 g of the ethylenamide was heated with an excess (25 g) of diethylamine in a sealed tube at 80-90° for 16 hours. The excess diethylamine was removed, and the product was distilled twice to yield 10.3 g (yield 67.5% of theoretical) of a substance with a b. p. of 168°/1.3; n_D^{20} 1.4655; d_4^{20} 0.9895. MR found 90.07 (calculated 90.10).

Found % P 9.90
$C_{14}H_{36}N_4O_2P$. Calculated % P 9.63

The addition of diethylamine to the diethylenamide of n-butylphosphoric acid. The method was similar to that described above. 15 g (yield 73% of theoretical) was obtained; b. p. 176°/1.0; n_D^{20} 1.4695; d_4^{20} 0.9761. MR found 99.97 (calculated 100.37).

Found % C 54.70; 54.64; H 11.37; 11.39; P 8.82; 8.84
$C_8H_{36}N_4O_2P$ Calculated % C 54.88; H 11.23; P 8.87

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ABSORPTION SPECTRA OF MOLECULAR COMPLEXES
OF BENZACRIDINE AND DIBENZACRIDINE DERIVATIVES

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(Presented by Academician B. A. Kazanskii, July 8, 1959)

The study of molecular complexes of the types [BK + AK]• or [BK⌒AK]•• with quinoline [1, 2] and acridine [3, 4] components has led to the conclusion that the tendency toward complex formation and the stability of the complexes is connected with the extent and area of the pi electron system of the planar molecule. With the aim of confirming this conclusion, we have studied molecular complexes of a component and a benzo derivative of acridine: 9-(p-Me$_2$N-styryl)-1,2-benzacridine (I, AK$_1$); 9-(p-Me$_2$N-styryl)-3,4-benzacridine (II, AK$_2$); 9-(p-Me$_2$N-styryl)-3,4,5,6-dibenzacridine (III, AK$_3$). 9-Methyl-10-benzylacridinium chloride (IV, BK$_1$) and 9,10-dimethyl-3,4,5,6-dibenzacridinium methyl sulfate (V, BK$_2$) were tested as VK components.
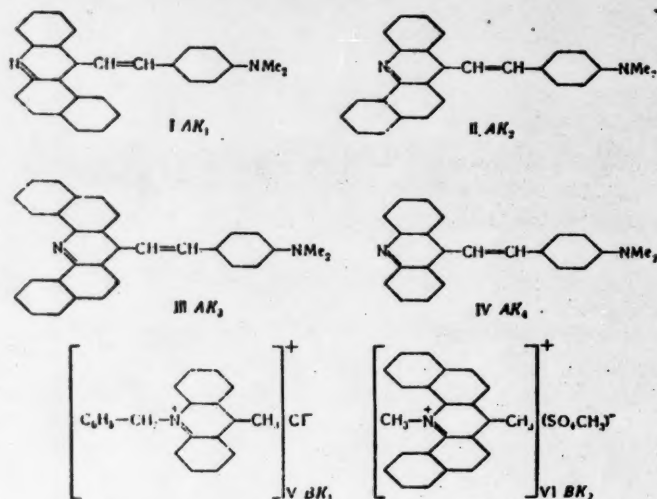
In order to eliminate the possibility of alcoholysis [4, 5] of the acridinium salt with the formation of HX [4] and subsequent addition of the HX to the AK$_1$, AK$_2$, etc. type component, 1,2-dichloroethane (DCE), appropriately purified, was used as the solvent. It is preferred over CHCl$_3$.

In comparison with 9-(p-Me$_2$N-styryl)acridine (IV, AK$_4$) (λmax 434 mμ) [3,4], when compound I, II, or III was the component, we observed a hypsochromic shift: $\Delta\lambda$ = −45, −18 and −33 mμ (Table 1, Nos. 1, 2, 3).

• BK—a complex electrophilic component composed of an electrophilic chromophore B (C= N+) and a π-electron system of a heterocycle, K. AK—a complex electron-donor component composed, correspondingly, of an electron-donor chromophore A = NMe$_2$ (Me= CH$_3$) [1].

•• The arc ⌒, a symbol of conjugation, denotes a partial π-bond, an exo-ρ-bond in the present case [1,5].

TABLE 1

Comparison of the Absorption Spectra of AK-Type and BK-Type Components with Spectra of Molecular Complexes of the Type [AK⌢BK] and of the Corresponding Dyes A−K−B

Expt. No.	Structure and component ratio	Solvent	C, mole/liter	Absn. bands of dye and complex		Absn. bands of component	
				λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
1	AK_1 (I)	C_2H_5OH	$1 \cdot 10^{-3}$			389	12070
2	AK_2 (II)	$CHCl_3$	$1 \cdot 10^{-3}$			416	17720
3	AK_3 (III)	CH_2ClCH_2Cl	$1 \cdot 10^{-3}$			401	25360
4	[1 AK_1+1 BK_1]	C_2H_5OH	$1 \cdot 10^{-3}$	557	8840	389	24635
5	[1 AK_1+1 BK_1]	C_2H_5OH	$1 \cdot 10^{-5}$	Нет	0	390	15480
6	[1 AK_1+1 BK_1]	$CHCl_3$	$1 \cdot 10^{-2}$	535	8770	388	19470
7	[1 AK_1+1 BK_1]	$CHCl_3$	$1 \cdot 10^{-5}$	514	4490	390	20575
8	[1 AK_1+1 BK_1]	CH_2ClCH_2Cl	$5 \cdot 10^{-6}$	542	5835	387	17000
9	[1 AK_2+1 BK_1]	CH_2ClCH_2Cl	$2,5 \cdot 10^{-6}$	568—570	4000	386	16800
10	[1 AK_2+1 BK_1]	$CHCl_3$	$1 \cdot 10^{-4}$	555	3990	386	25270
11	[1 AK_3+1 BK_2]	CH_2ClCH_2Cl	$5 \cdot 10^{-5}$	628	96	397	21600
12	$A-K-B$ IXa	0,006 N HCl in C_2H_5OH	$0,25 \cdot 10^{-3}$	558	11650	404	14110
13	$A-K-B$ IX6	CH_2ClCH_2Cl	$1 \cdot 10^{-3}$	561	5840	415	12360
14	$A-K-B$ Xa	0,006 N HCl in C_2H_5OH	$0,5 \cdot 10^{-4}$	574	11410	389	4745
15	$A-K-B$ X6	CH_2ClCH_2Cl	$1 \cdot 10^{-3}$	599	9910	420	13760
16	$A-K-B$ XI	0,001 N HCl in $CHCl_3$	$1 \cdot 10^{-3}$	605	12	400	20360
17	BK_1 (V)	CH_2ClCH_2Cl	$1 \cdot 10^{-3}$			403	6300
18	BK_2 (VI)	CH_2ClCH_2Cl	$1 \cdot 10^{-3}$			427	2140

The hypsochromic shift was caused by a weakening of the conjugation effect ($AK_3 > AK_2$) as a result of nullification of one or two of the extra rings. In the case of (I), there is also disruption of coplanarity.

A very interesting observation was made during the study of the spectra of the molecular complex [$AK_1 \frown BK_1$] (Table 1, Nos. 4-8, 9, 10): at C = $1 \cdot 10^{-5}$ mole/liter in alcohol, a complex was not formed. The complex formed to a considerable extent in $CHCl_3$ at C = 10^{-5} mole/liter: ϵ = 4490 (λ_{max} 514). The complexes were still more stable in DCE: [$AK_1 \frown BK_1$] even at $5 \cdot 10^{-6}$ mole/liter ϵ = 5835 (λ_{max} 542 mμ), and for [$AK_2 \frown BK_1$] at $2,5 \cdot 10^{-6}$ mole/liter ϵ = 4000 (λ_{max} 568—570 mμ) (Table 1, Nos. 8 and 9). We note that almost no complex was formed from AK_4 at A C = $2 \cdot 10^{-5}$ (ϵ = 75) [4]. With [$AK_3 \frown BK_2$] (Table 1, No. 11, Fig. 3), there was an unexpectedly large bathochromic effect: at C = $5 \cdot 10^{-5}$ mole/liter, λ_{max} 628 mμ, but the stability of the complex was low (ϵ = 96).

The existence of molecular complexes of AK_1 and AK_2 with BK_1 in DCE even at C = $2,5 \cdot 10^{-6}-5 \cdot 10^{-6}$ mole/liter confirms our assumption that the area of the π-system has significance with respect to the stability of the complex. In both of the cases λ_{max} 542 and 568 mμ there was a hypsochromic shift in comparison with AK_4 complexes [3, 4], and this is explained as a dispersion effect and, in the case of AK_1-, by steric effects. It is of particular theoretical interest that the maxima in the absorption spectra of solutions of the molecular complexes [$AK_1 + BK_1$], [$AK_2 + BK_2$], [$AK_3 + BK_2$] (Table 1, Nos. 4, 5, 8, 9, and 11) were located in the absorption region of the corresponding hemicyanines (IX), (X), (XI) (Table 1, Nos. 12-16; Figs. 1-3).

This confirms the earlier conclusion that λ_{max} for solutions of a complex of the type [$AK \frown BK$] can lie very close to λ_{max} for a dye with a conjugated AKB system containing similarly composed AK and BK systems superimposed on each other [2-5]. It is very important that in the experiments in which DCE was used, the possibility of alcoholysis was completely excluded. In this way it was shown that the cause of the emergence of color is just the formation of a molecular complex. New confirmation of this is the observation that if the colored solution is diluted with alcohol until the color of the complex has almost disappeared and is then cooled to −50° and −100°, then the appropriate color of the complex (violet-red or blue) again appears with a significant increase in ϵ in the region of λ_{max} [5].
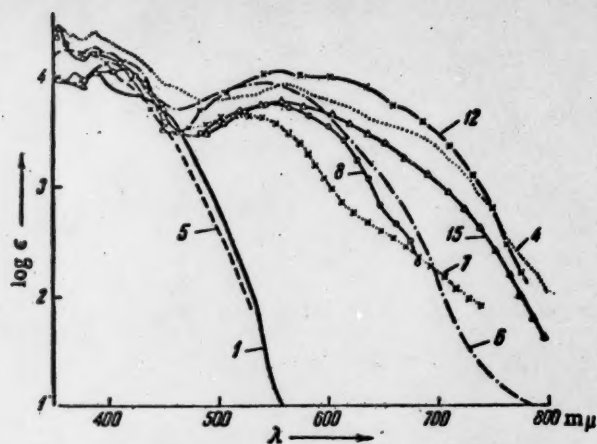
Fig. 1. Absorption spectra of complexes of 9-(p-Me$_2$N-styryl)-1,2-benzacridine (AK$_1$) with 9-methyl-10-benzylacridinium chloride (BK$_1$). The numbers on the curves correspond to the solution numbers in Table 1.
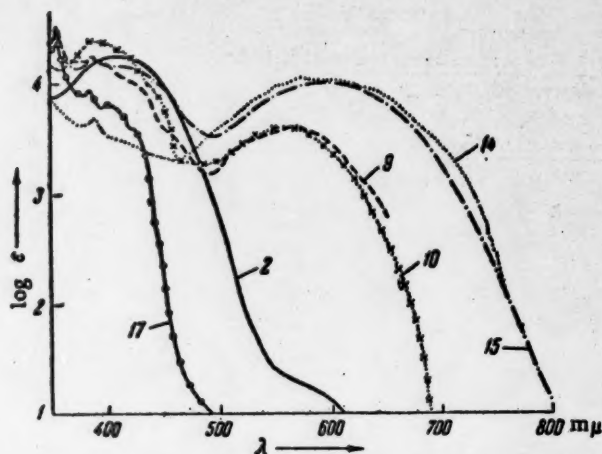
Fig. 2. Absorption spectra of complexes of 9-(p-Me$_2$N-styryl)-3,4-benzacridine (AK$_2$) with 9-methyl-10-benzylacridinium chloride (BK$_1$). The numbers on the curves correspond to the solution numbers in Table 1.

The deeper the color, the greater is the value of ϵ. Compounds I, II, III, and VI were prepared by the method of [8].

10-Ethyl-9-methyl-1,2-benzacridinium iodide (VII)—fine orange crystals (from alcohol), m. p. 286-287° (in a sealed capillary, with decomposition).

Found %: I 32.12; 32.10. C$_{20}$H$_{18}$NJ. Calculated %: I 31.78

$$\left[\text{R—N}\underset{BK}{\overset{Ah}{}}\text{—CH=CH—}\langle\text{benzene}\rangle\text{—NMe}_2\right]^+ X^-$$

a) R=H; X=Cl
b) R=C₂H₅; X=ClO₄

IX A·K·B

a) R=H; X=Cl
b) R=C₂H₅; X=ClO₄

X A-K-B

R=H; X=Cl

XI A-K-B
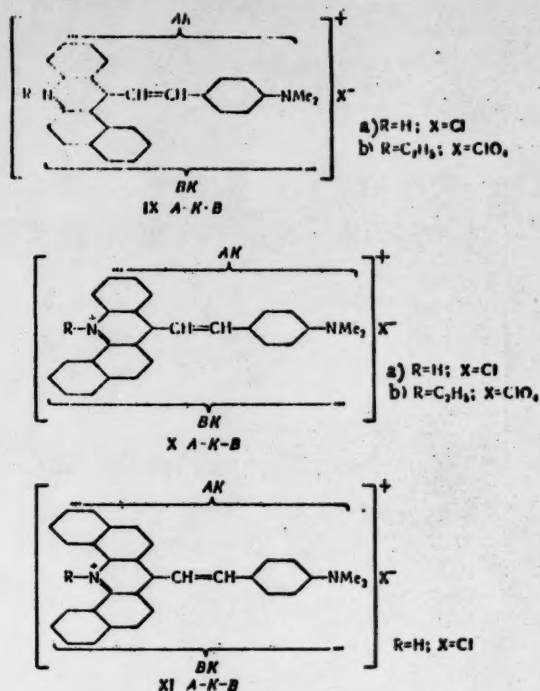
10-Ethyl-9-methyl-3,4-benzacridinium iodide (VIII)—fine, silky, orange needles (from alcohol), m. p. 290-292° (in a sealed capillary, with decomposition).

Found %: N 3.97; 3.88. $C_{20}H_{18}NI$. Calculated %: N 3,50

10-Ethyl-9-(p-dimethylaminostyryl)-1,2-benzacridinium perchlorate (IXb) was prepared from (VII). The dark green microcrystals melted at 206-208° (with decomposition).
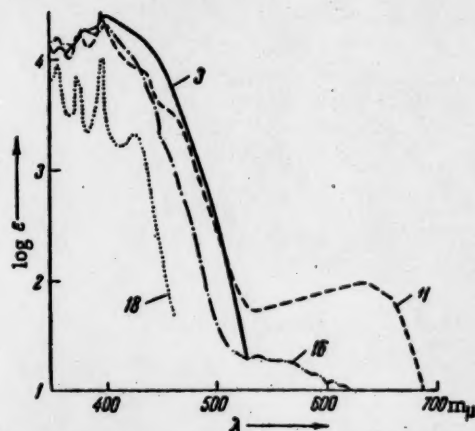
Fig. 3. Absorption spectra of complexes of 9-(p-Me₂N-styryl)-3,4,5,6,-dibenzacridine (AK₃) with 9,10-dimethyl-3,4,5,6-dibenzacridinium methyl sulfate (BK₂). The numbers on the curves correspond to the solution numbers in Table 1.

10-Ethyl-9-(p-dimethylaminostyryl)-3,4-benzacridinium perchlorate (Xb) was prepared from (VIII). The dark blue microcrystals melted at 226-227° (with decomposition). It was not possible to purify (IXb) and (Xb) completely.

Found %: Cl (IXb) 7,79; (Xb) 7,90. $C_{29}H_{27}N_2ClO_4$. Calculated %: Cl 7,05

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ESTERS OF PERFLUOROALKENYL-PHOSPHONIC ACIDS

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In 1948, G. Kh. Kamai attempted to carry out reactions between an ester of phenylphosphinic acid and tetrachloroethylene and tetrachloroethane, but individual products were not obtained [1]. Reactions of perfluoroolefins with dialkyl phosphites have been carried out only in radical-type reactions, which resulted in the formation of a mixture of telomeric fluorinated alkanephosphonic esters of the type $H(CF_2CF_2)_nPO(OR)_2$, where $n = 1 - 7$ [2].

$$n\ CF_2 = CF_2 + HPC(OR)_2 \rightarrow H(CF_2CF_2)_n\ PO(OR)_2.$$
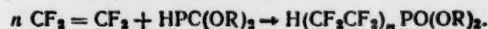
The ionic addition of neutral trialkylphosphite molecules to perfluoroolefins has not been known. It has now been found that trialkyl phosphites react comparatively readily with φ-olefins with the formation of esters of perfluoroalkenylphosphonic acids. The initial stage of this reaction is a nucleophilic attack by the positively polarized terminal carbon atom, which carries two fluorine atoms, with subsequent elimination of alkyl fluoride from the intermediately formed dipolar ion
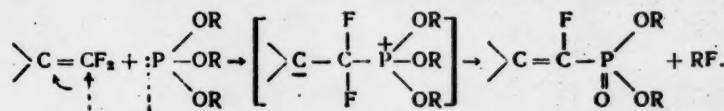
The diethyl esters of perfluorovinyl-, perfluoropropenyl-, perfluoroisobutenyl-, and perfluorocyclobutenylphosphonic acids were prepared. A similar type of reaction takes place during the interaction of trialkylphosphites with acrylic systems [3].
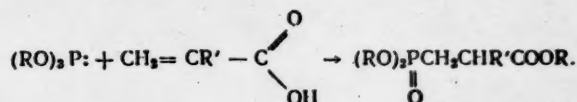
The activity of perfluoroolefins in the reaction with triethylphosphite decreases in the series:
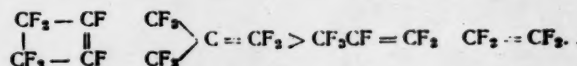
In addition to the ethyl esters of perfluoroalkenylphosphonic acids, a small amount of substances with low boiling points was formed during the interaction of perfluoroisobutylene and of perfluoropropylene with triethyl phosphite. In the case of tetrafluoroethylene, where there is no polarization of the double bond, the major product of the reaction is the diethyl ester of ethanephosphonic acid, which is formed as a result of isomerization of the triethyl phosphite under the influence of C_2H_5F:

$$P\ (OC_2H_5)_3 \xrightarrow{C_2H_5P} C_2H_5P\ (O)(OC_2H_5)_2.$$
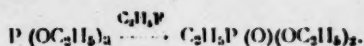
Only in the presence of a tertiary base (catalytic amounts), which decreases the rate of isomerization of the triethyl phosphite to the diethyl ester of ethanephosphonic acid, was it possible to obtain a 10-15% yield of the diethyl ester of perfluorovinylphosphonic acid.

TYPICAL EXPERIMENT

0.1 mole of triethyl phosphite and 0.3-0.4 mole of the φ-olefin were charged in a 250-ml autoclave. The temperatures and reaction times are shown in Table 1.

TABLE 1

Olefin	φ-cyclo-butylene	φ-isobuty-lene	φ-propylene	φ-ethylene
t, °C	0—5	90—100	130—140	160—170 (in the presence of NR$_3$)
Time, hours	10	8	8	8

TABLE 2

R$_f$	B.p.,°C	d_4^{20}	n_D^{20}	Yield	Calculated, %				Found, %			
					C	H	F	MR	C	H	F	MR
CF$_2$=CF—	81°/7	1,260	1,377	15	33,02	4,58	26,15	40,73	31,90	5,17	25,39	39,85
CF$_3$CF=CF—	83°/8	1,312	1,367	39	31,34	3,73	35,44	45,63	31,11	4,24	33,01	45,72
(CF$_3$)$_2$C=CF—	85°/8	1,400	1,365	66	30,19	3,10	41,82	50,53	29,90	3,27	41,66	50,75
CF$_2$—C— | | CF$_2$—CF	80°/5	1,351	1,392	21	34,28	3,56	33,92	49,51	34,18	3,55	33,65	49,49

At the conclusion of the reaction, the excess pressure was released, and the contents of the autoclave were distilled under vacuum. The diethyl ester of perfluorocyclobutenylphosphonic acid was thermally unstable, and could be distilled only under a good vacuum. In addition to the diethyl esters of the perfluoroalkenylphosphonic acids, in the experiments with φ-isobutylene and φ-propylene there were formed fractions with lower boiling points, 45°/8 mm for φ-isobutylene and 35°/8 mm for φ-propylene; the structures of these substances have not been established. After the first distillation, the diethyl esters of perfluoroisobutenyl- and perfluoropropenyl-phosphonic acids were dissolved in ether, washed with bicarbonate and with water, dried over magnesium sulfate, and distilled under vacuum. The diethyl ester of perfluorovinylphosphonic acid (b. p. 81°/8 mm) and the diethyl ester of ethanephosphonic acid (b. p. 75°/8 mm) distilled together. A fraction boiling at 73-85°/8 mm was collected during the first distillation, and it was poured into water; the diethyl ester of ethanephosphonic acid dissolved in the water. The remaining oil was dissolved in ether, and the ether solution was washed with water, dried, and distilled under vacuum. The physical constants and the results of the analyses of the esters of perfluoroalkenylphosphonic acids, R$_f$—P(O)(OC$_2$H$_5$)$_2$, are presented in Table 2.

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DEPENDENCE OF C_5-DEHYDROCYCLIZATION RATE
OF PARAFFINS AND ALKYLBENZENES ON CONTACT TIME
AND TEMPERATURE

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On the basis of a large number of cases, it has now been shown that the dehydrocyclization of hydrocarbons over platinized carbon can proceed not with just the formation of a six-membered benzene ring (C_6-dehydrocyclization), but can also simultaneously yield products with a five-membered ring (C_5-dehydrocyclization). The C_5-dehydrocyclization products obtained from paraffins are cyclopentanes [1-7], while those obtained from alkylbenzenes having a side chain of not less than three carbon atoms are indane and its homologs [8, 9]. It was recently shown that the C_5- and C_6-dehydrocyclization reactions are independent of each other and take place simultaneously on the surface of the platinum catalyst. Their relative rates in each individual case apparently depend on the structural peculiarities of the original hydrocarbon.
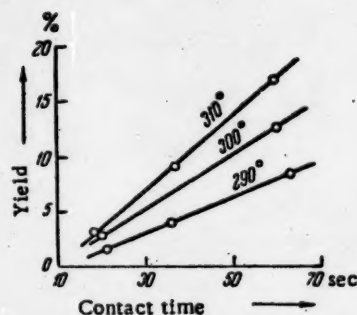
Fig. 1. Dependence of the yield of 1,1,3-trimethylcyclopentane from isooctane on contact time and temperature.

In order to obtain some information on the mechanism of these reactions, it appeared to be of interest to investigate the kinetics of C_5-dehydrocyclization and to compare them with the kinetics of C_6-dehydrocyclization, which we previously studied over a platinum catalyst [11]. The present paper presents the results of the first investigations carried out for this purpose. The most satisfactory subjects for such work are hydrocarbons which yield only one C_5-dehydrocyclization product. Therefore, we selected isooctane (2,2,4-trimethylpentane), n-hexane, and n-propylbenzene, which form respectively 1,1,3-trimethylcyclopentane, methylcyclopentane, and indane. The selection of isooctane and n-hexane was not dictated solely by the fact that one is highly branched and the other has a normal structure. Another difference was no less important: the first contains only five carbon atoms in a straight chain and cannot undergo C_6-dehydrocyclization, while the other has six carbon atoms in a straight chain, and both courses of reaction are possible for this compound.

As briefly mentioned earlier [6], the C_5-dehydrocyclization rate of isooctane at 310° depends linearly on the contact time. In the present work, it was shown that the relationship is still linear at 290°, but the line has a lower slope. The linear relationship is probably also retained at intermediate temperatures. In such a case, the slope of the line increases with an increase in temperature (Fig. 1 and Table 1). Similar linear relationships were also observed for n-hexane and n-isopropylbenzene (Fig. 2 and Table 2). Therefore, it might be assumed that this is a general rule characteristic of C_5-dehydrocyclization. Such a relationship suggests that the number of molecules of the original substance reacting in unit time on a given portion of the catalyst at a given temperature does not depend within the range studied on contact time, nor consequently on feed rate. The correctness of this assumption
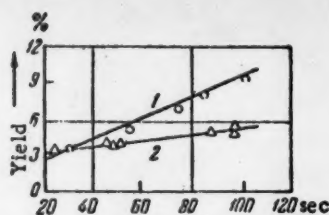
Fig. 2. Dependence of the yield of cyclization products on contact time: 1 — n-Propylbenzene; 2 — n-hexane.
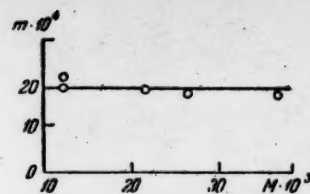
Fig. 3. Dependence of the number of moles of isooctane reacting (m) on the number of moles fed (M) at 310°.

was confirmed. Indeed, as may be seen from the data presented in Fig. 3 and Table 3, within the limits of experimental error, the number of molecules reacting per unit time remained practically constant, even with a three-fold increase in the isooctane feed rate. Hence, one concludes that the concentration of isooctane on the surface of the catalyst remained constant with an increase in contact time in the range studied, and the reaction was kinetically zero order. Obviously, this conclusion can be extended to the other hydrocarbons studied here, and can also be extended to other compounds which undergo C_5-dehydrocyclization.

TABLE 1

Dependence of the Yield of 1,1,3-Trimethylcyclopentane on Contact Time and Temperature

Expt. No.	Temp. °C	Space rate, hr^{-1}	Contact time, sec	Yield, %
106	290	0.20	62	8.5
105	290	0.36	36	4.0
104	290	0.60	21	1.5
98	300	0.20	60	12.7
103	300	0.60	21	2.7
96	310	0.20	59	16.9
108	310	0.32	37	9.0
109	310	0.68	18	3.0

TABLE 2

Dependence of the Yield of Cyclization Products on Contact Time

Expt. No.	Space rate, hr^{-1}	Contact time, sec	Catalyzate properties		after chromatographing	Yield of cyclization products, %
			before chromatographing		after chromatographing	
			n_D^{20}	d_4^{20}	n_D^{20}	
n-Hexane						
7	0.39	24	1.3778	—	1.3761	3.4
10	0.39	24	1.3778	—	1.3761	3.4
1	0.21	45	1.3778	—	1.3764	4.2
6	0.20	47	1.3788	—	1.3763	4.0
3	0.19	51	1.3781	—	1.3764	4.2
4	0.11	87	1.3793	—	1.3767	5.0
12	0.10	97	1.3793	—	1.3767	5.0
5	0.10	97	1.3794	—	1.3768	5.3
8	0.10	97	1.3794	—	1.3768	5.3
n-Propylbenzene						
31	0.35	30	1.4937	0.8657	—	3.6
30	0.19	54	1.4943	0.8672	—	5.0
35	0.14	73	1.4952	0.8680	—	7.0
34	0.12	84	1.4958	0.8689	—	8.1
36	0.10	101	1.4962	0.8693	—	9.1*

* Bromine number 0.35

During our study of the dependence of C_5-dehydrocyclization rate on temperature, it was found that the experimental data were satisfactorily described by the Arrhenius equation. This permitted determination of the apparent activation energies (Q) and preexponential factors (k_0) for this reaction in the paraffin and aromatic series without determination of the reaction rate constants. The data obtained (Fig. 4 and Table 4) show that the difference in the structures of the paraffinic hydrocarbons is not reflected in the magnitude of the activation energy for C_5-dehydrocyclization (Q = 20.0 ± 0.5 kcal /mole for both n-hexane and isooctane). These values are fairly close to the value obtained for the apparent activation energy of C_5-dehydrocyclization of diisobutyl (Q = 16 kcal /mole) [11]. It is possible that this is connected with the operation of similar mechanisms in the two reactions.

The presence of a benzene ring in the molecule of the original hydrocarbon had an appreciable effect on the value of the C_5-dehydrocyclization activation energy; it increased to 27.5 ± 0.5 kcal /mole. The preexponential factor in the Arrhenius equation was significantly higher for n-propylbenzene ($k_0 = 1.1 \cdot 10^{11}$) than for the paraffins

($k_0 = 1.1 \cdot 10^8$ for n-hexane and $5.8 \cdot 10^8$ for isooctane). This is obviously explained by the greater adsorption of aromatic compounds than of paraffins on the active centers of the platinum catalyst.
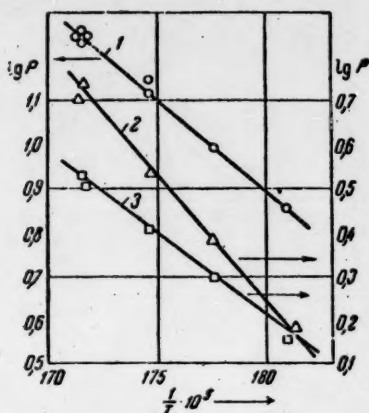
Fig. 4. Arrhenius equation lines for C_5-dehydrocyclization: 1) Isooctane; 2) n-propylbenzene; 3) hexane.

It is curious that our experimental values for the activation energies of C_5-dehydrocyclization are not in agreement with the value of the energy barrier for the closure of a five-membered ring obtained by Levi and Balandin on the basis of theoretical calculations [12]. Without going into the details of these calculations, we may point out that all of the considerations of these authors were based on the assumption of closure of the five-membered ring on a platinum doublet. However, the doublet mechanism for C_5-dehydrocyclization is not the only possible one, and it still requires confirmation. It could be that this original presumption led the above authors to results which are not in agreement with our experimental data.

EXPERIMENTAL

Experimental method. The catalyst was platinized carbon (20% Pt) prepared by the method of Zelinskii and Turova-Polyak [13] and stabilized by passing isooctane over it for 30 hours. Catalyst activity remained practically constant over the duration of a series of experiments, as was confirmed from time to time by control tests under standard conditions. The experiments were carried out with 10 ml of catalyst in a flow system. The starting material was fed from an automatic burette at practically constant space rate (the space rate was 0.2 hours^{-1} during the determinations of activation energies). The temperature was maintained constant over the course of an experiment within a deviation of $\pm 1.5°$. The duration of an experiment was 2-3 hours. The course of the reaction was checked periodically (after each 15 minutes) by taking a sample of the catalyzate and measuring its index of refraction. Calculation of the yield of cyclic reaction product was based on the assumption of additivity of the changes in index of refraction when the appropriate hydrocarbons are mixed [3, 8].

TABLE 3

Dependence of the Number of Moles of Isooctane Reacting (m) on the Number Fed (M) at 310°

Expt. No.	Space rate hr^{-1}	$M \cdot 10^3$	Over-all yield of 1,1,3-tri-methylcyclo-pentane, %	$m \cdot 10^4$
208	0.20	12.1	18.6	22.3
211	0.20	12.1	16.3	19.5
207	0.36	21.8	8.8	19.2
209	0.44	26.6	6.5	17.3
212	0.61	36.9	4.6	17.0

The catalyzate obtained during the first hour was discarded, since it differed in physical constants from the remainder of the catalyzate. Apparently, hydrogen adsorbed on the catalyst has an effect during this period, and the hydrogen is later displaced by the feed hydrocarbon. The index of refraction was determined on the total catalyzate collected in the ensuing period, and, in the case of alkylbenzene cyclization, the yield of indane hydrocarbons was calculated from this value. In the case of paraffin hydrocarbon cyclization, the catalyzate was chromatographed in a small silica-gel column (volume of about 1 ml) for separation of the paraffin−naphthene fraction from the aromatics and traces of olefins.

The yield of cyclopentane hydrocarbons was determined from the index of refraction of the paraffin−naphthene fraction, and the aromatic yield was determined from the difference in the index of refraction of the catalyzate before and after chromatographing. Since the aromatics obtained during cyclization of the isooctane were formed from 1,1,3-trimethylcyclopentane by a secondary reaction [10], the true yield of the latter was calculated by adding the yield of aromatics to the trimethyl-pentane yield. In the case of n-hexane, this could not be done, since it may be assumed that most of the benzene obtained was formed directly by C_6-dehydrocyclization simultaneously with the formation of the methylcyclopentane [10]. The yield of the latter was determined refractometrically.

TABLE 4

Dependence of the Yield of Cyclization Products on Temperature (Space Rate, 0.2 hours^{-1})

Expt. No.	Temp., °C	n_D^{20} before chromatographing	n_D^{20} after chromatographing	Yield of cyclization products, %	Expt. No.	Temp., °C	n_D^{20} before chromatographing	n_D^{20} after chromatographing	Yield of cyclization products, %
					144	310	1.3957	1.3948	17.9
					146	310	1.3957	1.3948	17.9
					148	310	1.3952	1.3948	17.4
					158	310	1.3956	1.3949	16.2
		n-Hexane							
16	280	1.3758	1.3754	1.4			**n-Propylbenzene**		
15	290	1.3760	1.3756	2.0	39	280	1.4928	—	1.5
17	300	1.3763	1.3758	2.6	42	290	1.4928	—	1.5
13	310	1.3771	1.3761	3.4	38	290	1.4932	—	2.4
14	310	1.3770	1.3761	3.4	41	300	1.4937	—	3.5
		Isooctane			37	310	1.4946	—	5.4
154	280	1.3930	1.3928	7.2	40	310	1.4945	—	5.2
152	290	1.3937	1.3933	9.9	43	310	1.4946	—	9.4
150	300	1.3948	1.3942	14.6					
156	300	1.3943	1.3940	13.3					

Feed hydrocarbons. The n-hexane and isooctane used in the present work were separated from the commercial products by silica-gel chromatography and rectification in highly efficient columns. Synthetic n-propylbenzene [9] was used. The constants of these hydrocarbons were not essentially different from the most reliable literature values [14]. All of the experimental data obtained on the dependence of the yield of cyclization products on contact time and on temperature are presented in Tables 1-4 and in Figs. 1-4.

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•Original Russian pagination. See C. B. translation.

ON THE LOWER CONCENTRATION LIMIT IN THE SELECTIVE
EXTRACTION OF INORGANIC SUBSTANCES

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In studies of the region of stratification of multicomponent systems, the existence of a lower concentration limit (threshhold) in the selective extraction of inorganic substances with organic solvents has been established beyond doubt [1, 2]. It should be remarked that this lower limit is observed for different extractable salts (uranyl and thorium nitrates), solvents (diethyl ether, tributyl phosphate, normal and isoamyl alcohols, and Chlorex), and salting-out agents (ammonium, aluminum, and zinc nitrates). Moreover, by increasing the concentration of uranyl and thorium nitrates it is possible to go beyond the threshhold limits without the introduction of salting out agents. or acids.
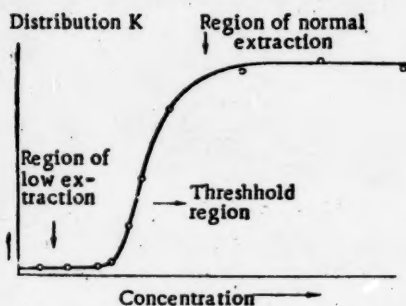
Fig. 1

K_{dist} for nitrates of trivalent rare earth elements is low, lower than for the threshhold region, regardless of the concentration. Only upon the introduction of salting-out agents or acids (10-12 N) do these substances begin to appear in the tributyl phosphate solvent in interesting amounts. For nitrates of the alkali and alkaline earth elements (regardless of the concentration of the salts, of the salting-out agents, or of the acid) transfer into the organic phase is ordinarily characterized by values of K_{dist} thousands of times lower than those of, for example, uranyl, thorium, and other nitrates. This determines the greater purification and the method used for separation during extraction. It is difficult to select a selective solvent for this class of salts.

A lower concentration threshhold (limit) was established by V. G. Khlopin [3] for the case of distribution between a liquid and solid phase (anomalous mixed crystals*). He pointed out that significant and relatively constant values of K_{dist} or D** are observed at higher threshholds and, particularly, higher concentrations of the distributable substance. The latter observation is in complete agreement with our observations established for distribution between two immiscible liquids [1]. Figure 1 shows the region of low extraction, the threshold region, and the region of normal extraction for the case of distribution between two liquids.

The appearance of a threshhold region during distribution between a solution and anomalous mixed crystals, i. e. a sharp increase in K_{dist} with concentration, was explained by V. G. Khlopin [3] on the basis that equilibrium between phases is established not by the individual ions, but with participation of the entire ionic complex sufficient for the formation of a unit cell. There is hardly any objection to the transfer mechanism proposed by V. G. Khlopin for distribution between two immiscible liquids.

Thus, it is generally recognized that undissociated molecules of the distributable salt are extracted into the organic phase in the form of solvates or hydrate-solvates. It is well known that the majority of organic phases

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* Apparently refers to a solid precursor to the true mixed crystals (true solid solution); cf. C. A. 24, 1005 (1930).
** Apparently "crystallization coefficient;" cf. C. A. 44, 9267 g, (1950). [Translator].

containing inorganic salts do not conduct a current; i. e. these solutions contain no ions or conducting complexes. However, up to the present there has been no basic conclusion formed regarding a molecular (group) mechanism for transfer into the organic phase; i. e. the inevitable appearance of a region of low extraction and a threshhold region has not been proposed by analogy to anomalous solid solutions. All the basis required for the elimination of this inconsistency is available, and the experimental data presented above on the lower threshhold concentration during extraction shows directly the correctness of the above conclusion.

It is probably necessary to recognize an ionic mechanism for distribution in the region of low extraction, i. e. it is necessary to assume an insignificantly low transfer of ions from the aqueous into the organic phase. With an increase in the concentration of the extractable salt, there is an increase in the probability of the appearance of molecules (or groups of molecules) in the aqueous phase, extraction begins to increase, and, finally, at some concentration a molecular (group) mechanism becomes predominant, and the threshhold region appears. For trivalent lanthanides, this mechanism develops only in the presence of a salting-out agent or an acid (10-12 N).

The region of normal extraction can only formally follow the simplest distribution law (see Fig. 1), since ions predominate in the aqueous phase, while undissociated molecules in the form of solvates or hydrate-solvates predominate in the organic phase.

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• In Russian.

ON THE ADDITION OF HYDRISILANES
TO DIMETHYLVINYLETHYNYLCARBINOL
AND TO ITS CYANETHYLATION PRODUCT

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Several years ago, Petrov, Sadykh-Zade and Egorov [1] synthesized a series of trialkylvinylethynylsilanes, $-Si-C\equiv C-CH=CH_2$, and established that lithium alkyls add to silicohydrocarbons of this type at the double bond, while two bromine atoms and also two hydrogen atoms add across the triple bond forming easily polymerized compounds of the butadiene type. More recently 1-trialkylsilylbutadienes were obtained from the secondary alcohol, which was synthesized by Grignard reaction [2].

$$\searrow Si-CH_2MgX + \overset{O}{\underset{H}{C}} - CH = CH_2 \rightarrow \searrow SiCH_2 - CHOH - CH = CH_2 \rightarrow$$

$$\rightarrow \searrow Si - CH = CH - CH = CH_2,$$
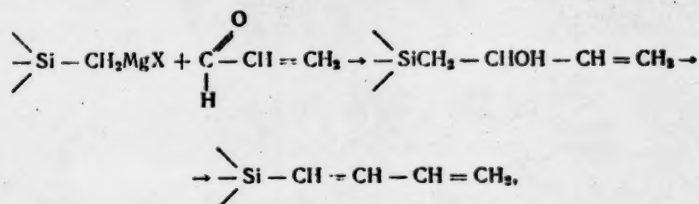
and 2-trialkylbutadienes were prepared according to [3]

$$(C_2H_5)_3SiH + HC \equiv C - \overset{CH_3}{\underset{}{C}}(OH) - CH_3 \rightarrow CH_2 = \overset{Si(C_2H_5)_3}{\underset{CH_3}{C}} - C(OH) - CH_3 \rightarrow$$

$$\rightarrow H_2O + CH_2 = \overset{CH_3}{\underset{Si(C_2H_5)_3}{C}} - C = CH_2.$$
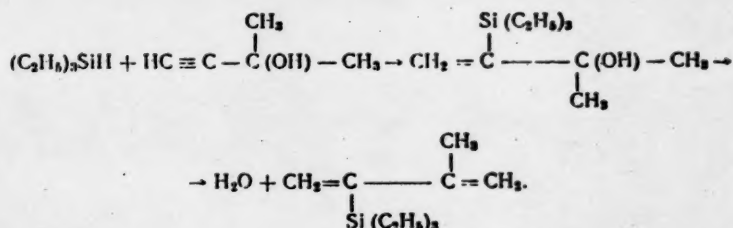
Finally, we recently found conditions (H$_2$PtCl$_6$ catalyst, moderate temperature) [4] under which methyldichlorosilane adds to vinylacetylene (with yields of up to 40-50% based on the amount of silane reacting) according to the scheme:

$$CH_3HSiCl_2 + HC \equiv C - CH = CH_2 \rightarrow Cl_2Si - CH = CH - CH = CH_2.$$
$$\underset{CH_3}{|}$$
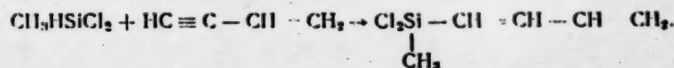
In addition to the latter reaction, it appeared to be of interest also to study the addition of hydrisilanes to the tertiary alcohol dimethylvinylethynylcarbinol and to its cyanethylation product, which also contains a vinyl-ethynyl radical:

$$\left(CH_2 = CH - C \equiv C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH; \ CH_2 = CH - C \equiv C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - O - CH_2 - CH_2 - CN \right).$$
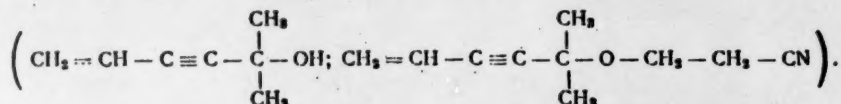
We also included in the scope of the present investigation a study of the nature of the addition of various hydrisilanes to the indicated disubstituted acetylenic compounds. As is well known [5], two molecules of a hydrisilane add to acetylene to form a saturated compound:

$$HC \equiv CH + 2 HSiCl_3 \rightarrow Cl_3SiCH_2 - CH_2SiCl_3.$$

Hydrisilanes (CH_3HSiCl_2) add primarily in a mole-for-mole ratio to a monosubstituted acetylene. We hoped that the greater steric hindrance peculiar to disubstituted acetylenic compounds—the alcohol and its cyanethylation product—would permit us to carry out the addition of only one molecule of hydrisilane across the triple bond and thereby to obtain higher yields of butadiene-type compounds containing a silicon atom. Our expectations were fulfilled, and we were able to add not only triethylsilane, but also methyl- and ethylchlorosilanes to the alcohol and to its cyanethylation product; the reaction proceeded with yields of up to 60% and spectroscopic analysis of the products showed that the hydrisilanes added across the triple bond forming readily polymerizable butadiene-type compounds.

$$CH_2 = CH - C \equiv C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH + (C_2H_5)_3 SiH \rightarrow CH_2 = CH - C = CH - \underset{\underset{Si(C_2H_5)_3}{|}}{\overset{}{}} \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - OH; \quad (1)$$

$$CH_2 = CH - C \equiv C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OCH_2 - CH_2CN + C_2H_5HSiCl_2 \rightarrow$$

$$\rightarrow CH_2 = CH - C = CH - \underset{\underset{C_2H_5SiCl_2}{|}}{\overset{}{}} \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - OCH_2 - CH_2CN; \quad (2)$$

$$CH_2 = CH - C \equiv C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OCH_2CH_2CN + CH_3HSiCl_2 \rightarrow$$

$$- CH_2 = CH - C = CH - \underset{\underset{CH_3SiCl_2}{|}}{\overset{}{}} \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - OCH_2CH_2CN. \quad (3)$$
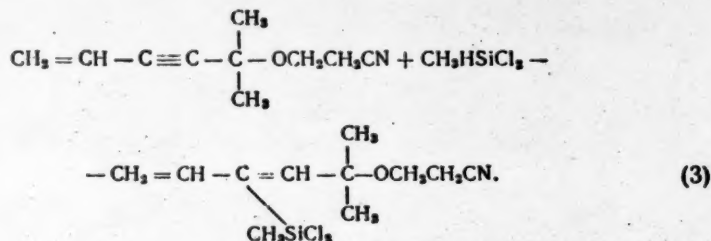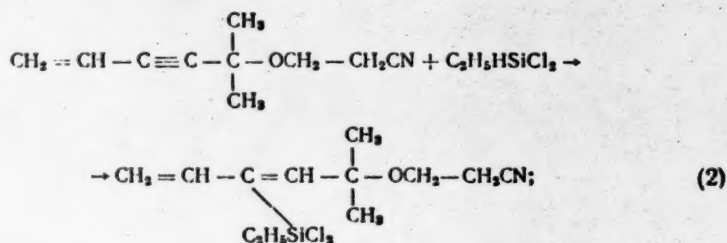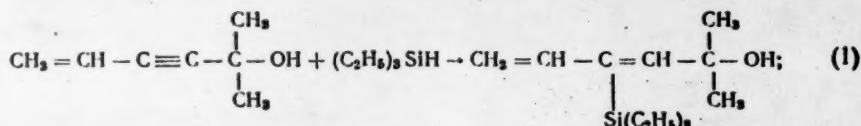
The monomers obtained according to Equations (2) and (3) proved to be particularly interesting. They were synthesized from available hydrisilanes, and they underwent not only polymerization, but also polycondensation reactions, after hydrolysis. Dehydration of the silicon-containing alcohol obtained according to Equation (1) yielded the first representative of organosilicon trienes 2-methyl-4-triethylsilyl hexatriene-1,3,5.

$$CH_2 = CH - C = CH - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - OH \xrightarrow[T]{KHSO_4} H_2O + CH_2 = CH - C = CH - \underset{Si(C_2H_5)_3}{\overset{\overset{CH_3}{|}}{C}} = CH_2.$$
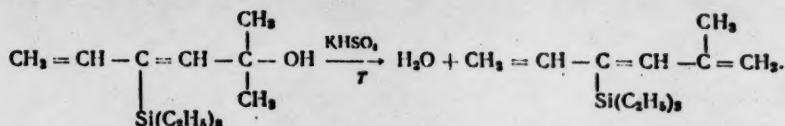
The authors take this opportunity to express to Yu. P. Egorov and L. A. Leites their appreciation for taking the spectra of these compounds.

EXPERIMENTAL

2-Triethylsilylbutadienyldimethylcarbinol.

$$CH_2 = CH - C = CH - \underset{\underset{Si(C_2H_5)_3}{}}{\overset{\overset{CH_3}{|}}{C}} - \underset{CH_3}{\overset{\overset{|}{C}}{C}} - OH.$$
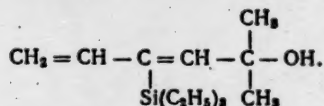
55 g (0.5 mole) of freshly distilled dimethylvinylethynylcarbinol and 0.5 ml of a 0.1 N solution of chloroplatinic acid were placed in a flask fitted with a stirrer and a condenser. 53 g (0.5 mole) of triethylsilane was added, with stirring, over a period of 30 minutes. During the addition of the silane, the temperature of the reaction mixture rose to 39° owing to the exothermic heat of the reaction; after the addition, the contents of the flask were heated to 170°. The reaction products were vacuum distilled under a pressure of 1 mm, and the following fractions were collected:

Fraction I, 30-85°, 7 g; Fraction II, 85-85.5°, 70 g. The undistilled residue, 26 g, was a rubbery polymer which was soluble in organic solvents.

Fraction II, which boiled at 85-85.5° (1 mm), had the following properties: n_D^{20} 1.4861; d_4^{20} 0.8873; MR_{found} 72.56; MR_{calc} 73.27. The yield was 62%

$$\text{Found \%: C 69,18; 69,15; H 11,60; 11,39; Si 12,30; 12,57}$$
$$C_{13}H_{26}SiO. \text{ Calculated \%: C 68,95; \qquad H 11,56; \qquad Si 12,40}$$

Raman spectrum, in cm^{-1}: 235(1), 250(1), 298(2), 359(1), 512(4b), 598(4b), 630(1), 676(2), 723(3), 760(2), 775(2), 831(2), 907(5), 971(4), 1010(3db), 1148(7), 1193(3), 1230(4b), 1296(8), 1340(5b), 1378(2), 1458(7), 1614(20), 2874(83), 2905(3), 2395(3), 2962(4), 3000(2), 3077(4). Since the spectrum contained no lines assignable to a triple bond and since there was a very intense line at 1614 cm^{-1}, it can be definitely stated that the R_3Si added at the triple bond with the formation of a conjugated diene system. The spectrum contained typical frequencies for the $-CH=CH_2$ group—1296, 1410, 1614, 3000, and 3077 cm^{-1}—and also for a C_2H_5 attached to a silicon—970, 1010, 1230, and 300 cm^{-1}.

II. 3-Ethyldichlorosilyl-5,5-dimethyl-5-cyanopropoxy-butadiene-1,3.

$$CH_2 = CH - C = CH - \underset{\underset{C_2H_5SiCl_2}{}}{\overset{\overset{CH_3}{|}}{C}} - \underset{CH_3}{\overset{\overset{|}{C}}{C}} - O - CH_2 - CH_2 - CN.$$
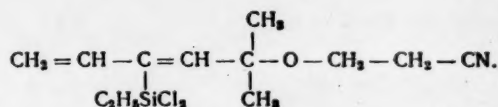
32.3 g (0.25 mole) of ethyldichlorosilane was added to 41 g (0.25 mole) of cyanopropoxydimethylvinylethynylcarbinol and 0.2 ml of an 0.1 N solution of H_2PtCl_6 in isopropyl alcohol; the mixture was stirred and heated (75°) during the addition. With an increase in the temperature of the reaction mixture to 90°, the reaction became violent (cooling was required), and the temperature of the flask contents rose to 140°. After distillation of the unreacted starting material, the remaining material, 68 g, was vacuum distilled at a pressure of 3 mm. A 61% yield of a fraction boiling at 150-151° (3 mm) was obtained; n_D^{20} 1.4865; d_4^{20} 1.0846; MR_{found} 77.46; MR_{calc} 76.49.

$$\text{Found \%: C 48,24; H 6,70; Si 9,91; Cl 23,74}$$
$$C_{12}H_{19}SiOCl_2N. \text{ Calculated \%: C 48,61; H 6,55; Si 9,57; Cl 24,29}$$

An infrared spectrum was taken in the 1600-2300 cm^{-1} region, and bands were found at 1608 cm^{-1}, which is characteristic of conjugated double bonds [6], and at 2244 cm^{-1}, which is characteristic of the $C \equiv N$ bond. The spectrum contained no bands characteristic of the $C \equiv C$ triple bond.

III. 3-Triethylsilyl-5,5-dimethyl-5-cyanopropoxy-pentadiene-1,3.

$$CH_2 = CH - C = CH - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - OCH_2CH_2 - CN.$$
$$\underset{Si(C_2H_5)_3}{|}$$
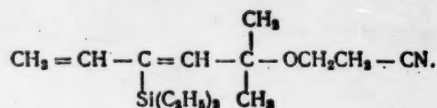
This compound was prepared by the addition of triethylsilane to the β-cyanoethyl ether of dimethylvinyl-ethynylcarbinol under the same conditions used in the preparation of II. The yield was 75%; b. p. 158° (3 mm); n_D^{20} 1.4840; d_4^{20} 0.9196.

Raman spectrum, $\Delta\gamma$, in cm^{-1}: 1241(0), 1305(1b), 1345(0), 1410(1), 1457(1), 1617(10b), 2247(1), 2871(3), 2735(1), 3038(1), 3105(1). The structure of this preparation was confirmed by the line at 1617 (10b), which is characteristic of conjugated double bonds, and by the line at 2947, which is characteristic of the $C \equiv N$ group. The spectrum contained no lines assignable to the $C \equiv C$ triple bond.

IV. 3-Methyldichlorosilyl-5,5-dimethyl-5-cyanopropoxy-pentadiene-1,3 was prepared under the conditions used for the preparation of II. The yield was 54%; b. p. 146-148° (4 mm).

Found %: Si 10.35
Calculated %: Si 10.03

V. 2-Methyl-4-triethylsilyl-hexatriene-1,3,5. 2-Methyl-4-triethylsilyl-hexatriene-1,3,5 was prepared by dehydration of 2-triethylsilylbutadienyldimethylcarbinol (I) under the influence of $KHSO_4$. The b.p. was 91° (at 3 mm); n_D^{20} 1.4920; d_4^{20} 0.8759. MR_{found} 68.70; $MR_{calc.}$ 68.85. The yield was 90%.

Found %: C 74.84; H 11.34; Si 13.04
$C_{13}H_{24}Si$. Calculated %: C 74.91; H 11.60; Si 13.47

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•Original Russian pagination. See C. B. translation.

ON THE STRUCTURE OF MATRINE

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Matrine, $C_{15}H_{24}ON_2$, was isolated by Nagai [1] in 1889 from the roots of Sophora flavescens (S. angusti-folia). In 1933, A. P. Orekhov and N. F. Proskurnina [2] found it in S. pachycarpa and in S. alopecuraides [3]. More recently, it has been found in other species of Sophora [4, 5]. Matrine is a strong monobasic acid and a ditertiary base. One of the nitrogens occurs in an $>N-CO-$ group, and the compound is distinguished from the remaining alkaloids of the $C_{15}H_xON_2$ series by its ability to form matrinic acid under the action of an alcoholic solution of KOH.

Kondo and co-workers [6-10] undertook a study of the structure of matrine, and as a result, they proposed formulas I and II as the most probable.
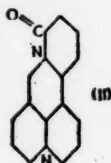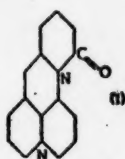
A number of authors have recently investigated the synthesis of matridine [11] and allomatridine [12] and the configurations of matrine and its isomer allomatrine, and formula II remains the preferred structure. However, a final choice between the two formulas presented above has not been made.

In our work, we attempted to establish the location of the $>N-CO-$ group and to cite this in support of one of the formulas. With this aim, we have studied the oxidative cleavage of the potassium salt of matrinic acid (potassium matrinate) under different conditions. The potassium matrinate was prepared by our previously described method [15].

Oxalic, cinnamic, and glutaric acids were isolated from the products of the oxidation of potassium matrinate (III) by potassium permanganate, but we were unable to obtain any nitrogen-containing compounds. Similar results were reported in the paper of Tsuda [9].

We then carried out the oxidation of potassium matrinate with chromium trioxide in 56% H_2SO_4, using the amount required to give the calculated amount of oxygen (15 atoms of oxygen per mole of potassium matrinate). In this case, after separation of the oxalic, cinnamic, and glutaric acids, we obtained D-lupininic acid in the form of an ester (IV), a readily distillable liquid with $[\alpha]_D$ of 17° (in methanol); the picrate melted at 151-152°, the hydrochloride at 200-201°, and the hydriodide at 268°. Saponification of the ester with 15% HCl yielded a crystalline hydrochloride, $C_{10}H_{18}O_2NCl$ (V), m. p. 275° (with decomposition), $[\alpha]_D$ (in methanol). The free amino acid, obtained from the hydrochloride, had the composition $C_{10}H_{17}O_2N$ (VI); it melted at 255°. The compositions and constants of the substances obtained were identical with those of the ethyl ester, the hydrochloride, and the free D-lupininic acid*.

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*One of us has developed a method for the separation of DL-lupininic acid.

The course of the reaction can be tespresented as follows:
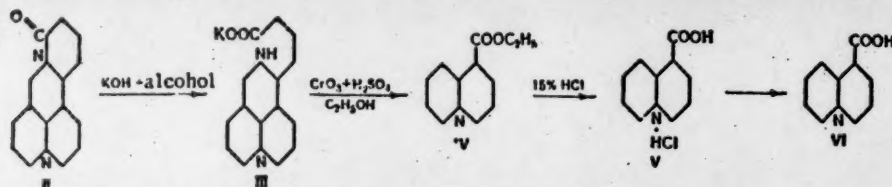
Oxidation of the same potassium matrinate with fuming HNO_3 (on a boiling water bath) and subsequent esterification yielded the ester of 5,7-quinolizidinedicarboxylic acid, $C_{15}H_{25}O_4N$ (VII), m. p. 56-57°, $[\alpha]_D$ 30.38 (acetone). The isomer of this acid — 7,9-quinolizidinedicarboxylic acid — has been prepared by oxidation of aphyllidine [16]. Saponification of (VII) with 15% HCl gave the crystalline hydrochloride of the amino acid $C_{11}H_{18}O_4NCl$ (VIII), m. p. 118°, $[\alpha]_D$ 49.57° (in water). Saponification of this product with 15% H_2SO_4 gave the free 5,7-quinolizidinedicarboxylic acid. It had the composition $C_{11}H_{17}O_4N$ (IX) and formed the sodium salt $C_{11}H_{16}O_4NNa$, m. p. 191-193° (with decomposition). It was noted that during melting of the hydrochloride (above 118°), the acid began to lose CO_2, being converted thereby into the hydrochloride of D-lupininic acid, which is characteristic. Hence, it may be concluded that 5,7-quinolizidinedicarboxylic acid is readily decarboxylated to the monobasic acid. It is probable that during the oxidation with chromium trioxide, (IX) was formed first and then decarboxylated to lupininic acid under the reaction conditions (temperature above 200°).

The course of the reaction can be represented as follows:
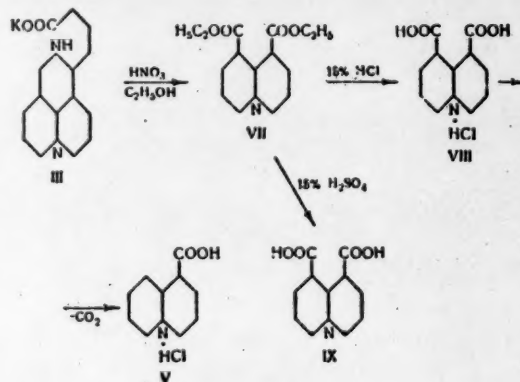
Thus, as result of the work described above, we have been led to a final conclusion as to the location of the >N—CO- group in the matrine molecule, and we have thereby confirmed the structure shown as formula (II) for this compound.

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CONTRIBUTION TO THE PROBLEM OF SALTS
OF PHOSPHOMOLYBDIC ACID OF HIGH BASICITY

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According to the theory due to Miolati [1] and Rosenheim [2], anions of heteropoly acids contain $R_2O_7^{2-}$-ions (R = Mo, W) as ligands; consequently, heteropoly acids must have high basicities, for example, $H_7[P Mo_2O_7)_6]$ and $H_8[Si(W_2O_7)_6]$. Generally, salts are formed from heteropoly acids of low basicity, $Na_3[PMo_{12}O_{40}] \cdot n H_2O$, $K_4[SiW_{12}O_{40}] \cdot n H_2O$, etc. It is well known that the preparation by Rosenheim and Pinsker [3] of heptabasic guanidine phosphomolybdate provided some of the grounds for the Miolati−Rosenheim theory. Beginning in 1940, E. A. Nikitina published a series of papers dealing with the preparation of salts of certain polybasic heteropoly acids [4, 5, 6] by the addition of the calculated amount of base to a solution of a salt of a less basic acid. In particular, she described the preparation of 4 and 11 substituted sodium phosphomolybdates [4].

On the other hand, theoretical considerations [7] and certain experimental data [8] have indicated that the addition of even small amounts of a base causes partial decomposition of heteropoly anions. In order to establish the nature of salts of so-called highly basic phosphomolybdic acids, we have studied the interaction of tribasic guanidine phosphomolybdate with guanidine carbonate and of tribasic sodium phosphomolybdate with sodium hydroxide. Preliminary to this work, the little-studied guanidine molybdates [3, 9, 10] were investigated, since the presence of these compounds as impurities could have a substantial effect on the composition and properties of the guanidine salts of heteropoly acids.

TABLE 1

Composition of the Products of the Interaction of Tribasic Guanidine Phosphomolybdate with Guanidine Carbonate

Prep. No.	Content, %					Ratio $CN_3H_6 : P_2O_5 : MoO_3 : H_2O$
	P_2O_5	MoO_3	N	CN_3H_6*	H_2O (by difference)	
1	0	79.63	12.23	17.20	3.17	2 : 0 : 3.80 : 1.22
	0	79.36	12.53	17.62	3.02	2 : 0 : 3.70 : 1.12
2	3.302	74.31	11.37	15.99	6.40	11.64 : 1 : 22.19 : 15.29
	3.311	74.64	11.34	15.66	6.39	11.37 : 1 : 22.23 : 15.22
3	2.560	72.25	12.59	17.70	7.49	17.00 : 1 : 26.73 : 23.06
	2.405	73.25	—	—	—	1 : 30.00
4	2.935	71.23	12.77	17.95	7.88	14.70 : 1 : 23.03 : 21.18
	2.857	71.45				1 : 24.66

* The guanidine content was calculated from the amount of nitrogen found.

The interaction of a 20% solution of guanidine carbonate, heated to 45-55°, with molybdenum trioxide at a pH of about 7 gave the readily soluble normal guanidine molybdate $(CN_3H_6)_2MoO_4$, which was isolated without water of crystallization and which was characterized by the following indices of refraction: $n_p = 1.594$; $n_g = 1.710$. From x-ray pictures* obtained by the oscillating crystal method, it was found that this compound crystallizes in

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* All of the x-ray patterns were obtained with Ni radiation.

the rhombic system with the following unit cell parameters: $a = 6.94$ kX (prism axis), $b = 13.0$ kX, and $c = 51.0$ kX. Crystalline guanidine paramolybdate, $10CN_3H_5 \cdot 12MoO_3 \cdot 8H_2O$, was prepared by an exchange reaction between an 0.5 M solution of guanidine nitrate and a 10% solution of sodium paramolybdate at 75-80°; it was also prepared by acidification of a 5% solution of normal guanidine molybdate with 0.1 N HCl to a pH of 4.5.*
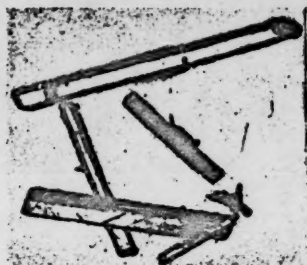

Fig. 1. Crystals of tribasic guanidine phosphomolybdate (150×).
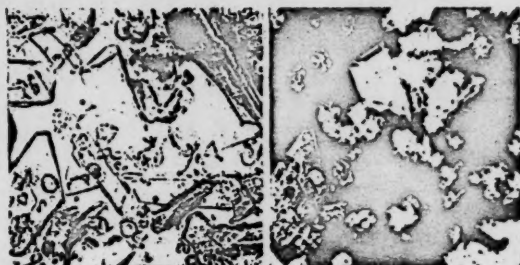
Fig. 2. A mixture of guanidine 11-phosphomolybdate and guanidine metamolybdate; the photograph was taken under the polarizing microscope. I— with parallel Nicols II—with crossed Nicols (600×).

Sparingly soluble guanidine metamolybdate, $2CN_3H_5 \cdot 4MoO_3 \cdot 1.5H_2O$, is formed by acidification of a 5% solution of normal guanidine molybdate with 5.5 N HCl to a pH of 1.9 or by the interaction of an 0.5 M solution of guanidine nitrate with a 10% solution of sodium metamolybdate preheated to 60°. Judging from the outward appearance of the preparation and from the x-ray and electron diffraction patterns, guanidine metamolybdate is an amorphous material. However, an optical investigation under a polarizing microscope (720×) showed that its fine grains could be spherulites. For the preparation of tribasic guanidine phosphomolybdate, the calculated amount of a 10% solution of guanidine carbonate was added to a 5% solution of phosphomolybdic acid (synthesized by the ether method [11]) at a temperature of 80-85°. According to the analytical data, the resulting bright yellow precipitate had the formula $6CN_3H_5 \cdot P_2O_5 \cdot 24MoO_3 \cdot 4H_2O$; the pH of the filtrate was 2.2.

Analysis of the preparation for phosphorus was carried out by the magnesium method. The molybdenum was separated as lead molybdate from the filtrate after precipitation of the magnesium ammonium phosphate. Nitrogen was determined by the Dumas or Kjeldahl method. Our measurements of the solubility of tribasic guanidine phosphomolybdate at 20 and 80° gave, respectively, 0.5 g and 2.5 g per 100 g of solution. This preparation contained even less combined water than that required by the formula $(CN_3H_6)_3H[P(Mo_2O_7)_6]$.

In conformity with the method of Rosenheim and Pinsker, a suspension of the tribasic salt in water (10g per 100 ml) was heated to boiling, and to this was added the calculated amount of guanidine carbonate solution; 3 moles of $(CN_3H_6)_2CO_3$ per mole of $6CN_3H_5 \cdot P_2O_5 \cdot 24MoO_3 \cdot 4H_2O$ The temperature was maintained in the range of 95-100°. The yellow suspension slowly disappeared, and the solution became green. Simultaneously, a white precipitate tinged with green formed. The solution was cooled to approximately 50°, and the precipitate was filtered in a heated funnel. This precipitate did not contain phosphorus, and its formula as determined by analysis approached that of guanidine metamolybdate (Table 1, No. 1). The filtrate had a pH of 3.12. After the solution had stood for 12 hours at room temperature, green crystals precipitated. The P-to-Mo ratio in these crystals was 1:11 (Table 1, No. 2). An investigation by means of the polarizing microscope showed that this substance was almost homogeneous. The indices of refraction of this material, determined by the immersion method, were $n_p = 1.808$; $n_m = 1.833$; $n_g = 1.846$.

The addition of 4 moles of guanidine carbonate per mole of $6CN_3H_5 \cdot P_2O_5 \cdot 24MoO_3 \cdot 4H_2O$ at a temperature of 75-80° led to rapid solution of the suspension (5 g/100 ml). After the solution had stood for 12 hours, it was possible to separate the pale-green finely crystalline powder (Table 1, No. 3) from the coarse green crystals (Table 1, No. 4) by decantation; the pH of the solution was 3.9. Analysis of the finely crystalline powder showed that it was a mechanical mixture, since parallel analyses gave significantly differing results. The phosphorus, molybdenum, and nitrogen contents of the coarsely crystalline product corresponded approximately to those reported by

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* The pH measurements were carried out with an LP-5 potentiometer.

Rosenheim and Pinsker for the heptabasic salt $(CN_3H_6)_7 \cdot [P(Mo_2O_7)_6] \cdot 8H_2O$. A study of this preparation under the polarizing microscope established that the majority of the green crystals were crystals of a salt with a P-to-Mo ratio of 1 : 11 contaminated with spherulites of guanidine metamolybdate. The pale-green, finely crystalline powder also proved to be a mechanical mixture of guanidine metamolybdate with a salt of the phosphomolybdic acid (1 : 11).

TABLE 2

Fractional Crystallization of the Products of the Interaction of Tribasic Sodium Phosphomolybdate with Sodium Hydroxide

Prep. No.	Content, %				Ratio $Na_2O : P_2O_5 : MoO_3 : H_2O$	Behavior with NH_4Cl
	P_2O_5	MoO_3	Na_2O	H_2O (by difference)		
1	3.304 3.328	80.54 81.54	4.386 4.321	11.71 10.81	2.19 : 1 : 23.61 : 27.46 2.97 : 1 : 24.16 : 25.62	Precipitate
2	3.480 3.449	80.38 80.05	— 4.726	— 11.78	1 : 22.77 3.14 : 1 : 22.89 : 26.04	Precipitate
3	4.061 4.015	75.18 74.96	5.340 5.857	15.40 15.18	3.02 : 1 : 18.26 : 29.91 3.34 : 1 : 18.42 : 29.83	No precipitate
4	3.682 3.651	74.40 74.64	— 5.751	— 15.96	1 : 19.93 3.61 : 1 : 20.16 : 34.49	No precipitate
5	3.320 3.357	80.52 80.67	4.515 4.516	11.65 11.46	3.11 : 1 : 23.92 : 27.69 3.08 : 1 : 23.70 : 26.03	Precipitate
6	1.970 2.097	73.10 74.14	— 8.400	— 15.36	1 : 36.52 9.17 : 1 : 34.86 : 57.77	No precipitate

Thus, the addition of even small amounts of guanidine carbonate causes the decomposition of the heteropoly anion with the formation of the guanidine salt of an acid with less than the limiting number of MoO_3 groups and guanidine metamolybdate.

The interaction of tribasic sodium phosphomolybdate with NaOH was also studied. The original salt had the composition $3.06Na_2O \cdot P_2O_5 \cdot 23.79MoO_3 \cdot 25.86H_2O$. The assumed product of its hydrolysis—sodium luteophosphomolybdate—was synthesized by the method described in reference [12]. The x-ray patterns corresponding to these salts are presented in Fig. 3 (Nos. 1 and 5). The sodium was determined as the ternary acetate $NaZn(UO_2)_3 \cdot (C_2H_3O_2)_9 \cdot 6H_2O$. The heteropoly anion was first precipitated with hydroxyquinoline. The excess of the hydroxyquinoline was removed by evaporation of the filtrate with a mixture of concentrated H_2SO_4 and HNO_3.

The calculated amount of a 0.25 N solution of NaOH (2 moles of NaOH per mole of $3Na_2O \cdot P_2O_5 \cdot 24MoO_3 \cdot nH_2O$) was added to a 30% solution of tribasic sodium phosphomolybdate. The pH changed from 1.4 to 1.8 as a result of the reaction. The resulting solution was evaporated under vacuum at 60° to the volume of the original salt solution, and was then subjected to fractional crystallization.

The solution was allowed to stand for a period of several days in a vacuum desiccator over concentrated H_2SO_4, and the resulting yellow crystals were separated from the mother liquor. Judging from the analysis (Table 2, No. 1) and the x-ray pattern (Fig. 3, No. 2), this fraction consisted of unreacted tribasic salt. Its solution gave a yellow precipitate with guanidine carbonate and NH_4Cl. The next fraction of crystals (Table 2, No. 2) obtained during the successive evaporation of the solution was a mixture of tribasic sodium phosphomolybdate and sodium luteophosphomolybdate (Fig. 3, No. 4). The third fraction was almost pure luteophosphomolybdate (Table 2, No. 3; Fig. 3, No. 6). An investigation of this fraction by immersion showed that it was homogeneous. The crystals had the following indices of refraction: $n_g = 1.801$; $n_p = 1.742$. A study of the fourth fraction (Table 2, No. 4) under the polarizing microscope showed that two phases were present. The major phase consisted of crystals of the luteo salt; the other phase was present in small amount. Judging from the analysis of the entire fraction, the fraction must have consisted of sodium metamolybdate, since the P-to-Mo ratio of the whole fraction was greater than 1 : 9, and was, in fact, approximately 1 : 10.

The residual mother liquor was allowed to stand for several additional days in the vacuum desiccator until it was completely evaporated. The resulting solid product was treated with acetone. The solution was evaporated at room temperature. The resulting dry residue was investigated. The results of the analysis and the x-ray patterns
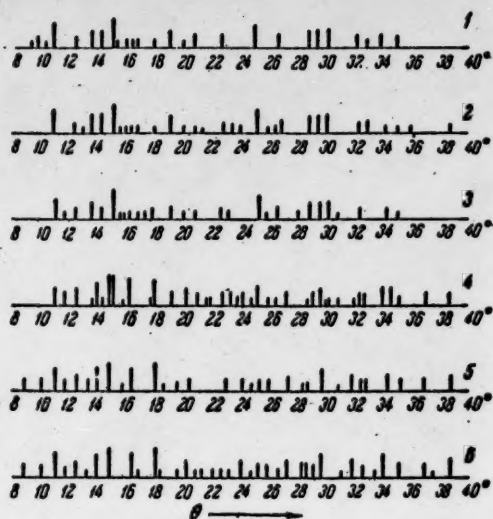
Fig. 3. Comparison of the Debye pattern of tribasic sodium phosphomolybdate with those of the products of its interaction with NaOH. 1—Tribasic sodium phosphomolybdate; 2—Preparation 1; 3—Preparation 5; 4—Preparation 2; 5—sodium luteophosphomolybdate; 6—Preparation 3.

showed that this preparation was identical to tribasic sodium phosphomolybdate containing the limiting number of MoO_3 groups (Table 2, No. 5; Fig. 3, No. 3). The acetone-insoluble portion (Table 2, No. 6) was characterized by a higher molybdenum content than that required by the limiting compound (ratio of P to Mo of 1:16). This was undoubtedly due to the presence of sodium metamolybdate as an impurity, since spherulites of guanidine metamolybdate were observed in the precipitate obtained by the action of guanidine nitrate. The interaction of the tribasic phosphomolybdate with sodium hydroxide evidently proceeds according to the scheme:

$$2(3Na_2O \cdot P_2O_5 \cdot 24 MoO_3 \cdot nH_2O) + 6NaOH \rightarrow$$
$$\rightarrow 2(3Na_2O \cdot P_2O_5 \cdot 18 MoO_3 \cdot nH_2O) +$$
$$+ 3 (Na_2O \cdot 4MoO_3 \cdot nH_2O).$$
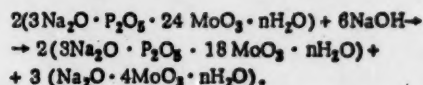
On the basis of the above date, it is possible to form the final conclusion that the existence of guanidine and sodium salts of highly basic phosphomolybdic acids has not been confirmed. Even with an insignificant increase in pH, cleavage of ligands of the inner sphere from the limiting heteropoly anion proceeds with the formation of metamolybdate and phosphomolybdates containing less than the limiting number of MoO_3 groups.

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THE INFRARED ABSORPTION AND POLARGRAPHIC BEHAVIOR
OF 2-NITRO- AND 2-HYDROXYIMINO-1,3-INDANDIONE

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The structure of nitro and nitroso derivatives of 1,3-indandione is of theoretical interest in view of the possibility that these compounds may exist in different valence structures. Bromine titration data obtained by K. Maier and the extremely high acidity of 2-nitro-1,3-indandione indicate that we are dealing with a nitronic acid in aqueous solutions [1, 2]. It has been shown by means of ultraviolet absorption spectra that the nitrodiketo form exists in solvents of low polarity, while in polar solvents, 2-nitro-1,3-indandione is completely dissociated, and the absorbing fragment is the anion, to which a mesomeric structure has been assigned [3]. 2-Hydroxyimino-1,3-indandione has a number of specific properties which have led to discussions of the question of whether this compound is the oxime of indantrione or 2-nitroso-1,3-indandione [4-7].

With the aim of determining the true structure, these compounds and certain of their salts were studied by infrared spectroscopy and polarography.

EXPERIMENTAL

The following compounds were investigated: 2-nitro-1,3-indandione (anhydrous, m. p. 110° C) and its dihydrate (m. p. 126°), the sodium salt of 2-nitro-1,3-indandione, 2-hydroxyimino-1,3-indandione, its sodium and tetraethylammonium salts, and the sodium salt of 2-methyl-1,3-indandione.

Since differences were observed between 2-hydroxyimino-1,3-indandione crystallized from water and this same compound crystallized from glacial acetic acid [7], both substances were studied: the i. r. spectra of the solid substances, and also the u. v. spectra and the polarograms of aqueous solutions proved to be identical. The melting points of these two substances were about 202-203° when the heating was slow; when the rate of heating was changed, we obtained a melting point of 213-214°. 2-Hydroxyimino-1,3-indandione recrystallized from dilute HCl was identical with respect to other properties, but had an i. r. spectrum which differed.

In certain cases, the i. r. spectra were taken with the substances suspended in vaseline oil, while in other cases, the substances were in solution. The wave numbers and the corresponding relative percent absorption are presented in Table 1. Polarograms were obtained with aqueous solutions of 2-nitro-1,3-indandione, 2-hydroxy-imino-1,3-indandione, the ethyl ester of indandionecarboxylic acid, and 1,3-indandione; the solutions were buffered with Britton-Patterson buffers, and the polarograms were obtained in the pH range of from 2 to 10 against a background of 0.1 N KCl. Equations relating the half-wave potential ($E_{1/2}$ to pH for the polarographic waves are presented in Table 2. The experimental work was carried out using IKS-12 spectroscopic apparatus and a Heyrovsky polarograph.

DISCUSSION OF RESULTS

In the double bond region of the i. r. spectrum of 2-hydroxyimino-1,3-indandione there was a vibration frequency due to the aromatic ring (1590 cm^{-1}), two C= O- group frequencies (1700 and 1735 cm^{-1}), and a C= N frequency (1610 cm^{-1}), which was shifted in comparison to similar frequencies for oximes (1626-1629 cm^{-1}) [8].

An intense band at 3180 cm^{-1} was assigned to the strongly associated OH group. Hence, it follows that 2-hydroxy-imino-1,3-indandione exists in a form represented by structure (I) with a strong intramolecular hydrogen bond; whence, the assumption follows that in the actual molecule, there is some redistribution of the electron density, which causes the shift of the C= N band and the increased acid properties (pK 5.75) as compared to oximes.

TABLE 1

The Most Characteristic Frequencies of the Compounds Studied

Compound	Medium	ν (cm^{-1})*
2-Nitro-1,3-indandione (anhydrous)	Paraffin oil	1445 (96); 1559 (100); 1616 (90); 1641 (45); 1658 (43); 1715 (87)
2-Nitro-1,3-indandione (dihydrate)	The same	1350 (86); 1594 (83); 1620 (81); 1638 (87); 1653 (89); 1692 (66)
Sodium salt of 2-nitro-1,3-indandione	The same	1358 (96); 1600 (91); 1643 (97); 1665 (98); 1698 (67);
2-Nitro-1,3-indandione (anhydrous)	Abs. C_2H_5OH	1600; 1641; 1663
2-Hydroxyimino-1,3-indandione	Paraffin oil	1593 (76); 1614 (52); 1698 (99); 1735 (84); 3180 (74)
2-Hydroxyimino-1,3-indandione (from CH_3COOH)	The same	1592 (70); 1610 (53); 1701 (87); 1734 (77); 3180 (73)
2-Hydroxyimino-1,3-indandione (from HCl)	The same	1588 (54); 1610 (41); 1701 (74); 1737 (47); 3250 (47); 3425 (44)
Sodium salt of 2-hydroxyimino-1,3-indandione	The same	1591 (70); 1661 (87)
Tetraethylammonium salt of 2-hydroxyimino-1,3-indandione	The same	1585 (76); 1655 (86)
Tetraethylammonium salt of 2-hydroxyimino-1,3-indandione	Acetonitrile	1598 (45); 1656 (81)
Sodium salt of 2-methyl-1,3-indandione	Paraffin oil	1500 (98); 1511 (98); 1569 (70); 1590 (50)

* The figures in parentheses are the relative percent absorption for the corresponding frequencies.

TABLE 2

Relationship between $E_{1/2}$ and pH for the polarographic waves (the values of E are with respect to saturated Hg_2Cl_2)

Compound	Eq. for first wave (entire pH interval) $E_{1/2}$	Eq. for second wave	Eq. for third wave	Eq. for fourth wave (alkaline medium) $E_{1/2}$
		acid medium $E_{1/2}$		
1,3-Indandione	—	—0,61—0,080 pH	—0,85—0,022 pH	—1,40
Ethyl ester of 1,3-indandionecarboxylic acid	—	—0,44—0,086 pH	—0,84—0,080 pH	—1,42
2-Hydroxyimino-1,3-indandione	+0,50—0,102 pH	—0,49—0,074 pH	—0,85—0,050 pH	—1,46
2-Nitro-1,3-indandione	—0,20—0,093 pH	—0,49—0,070 pH	—0,86—0,054 pH	—1,47

In addition, it is also possible for a modification with another type of hydrogen bond (probably intermolecular) to separate during crystallization of this substance from HCl. This explains the higher OH frequency at 3250 and 3420 cm^{-1}.

A frequency at 1655-1665 cm^{-1} is characteristic of salts of 2-hydroxyimino-1,3-indandione, which indicates significant deformation of all of the bonds in the anion and the approach of the mesomeric anion (II-III) to structure (II), since the characteristic frequency of the enolate anion of indandione β-diketones at 1510 cm^{-1} (as for the anion of 2-methyl-1,3-indandione) is not present in this case.

(I)   (II)   (III)
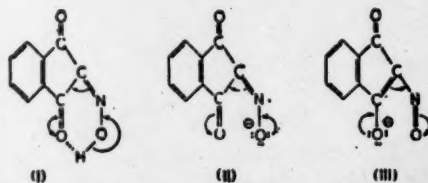
(It should be recalled that the two carbonyl groups are equivalent.)

The spectrum of solid anhydrous 2-nitro-1,3-indandione showed symmetrical and antisymmetrical vibration frequencies of the nitro group (1445 and 1560 cm^{-1}) as well as the vibration frequencies of the aromatic ring (1616 cm^{-1}) and the carbonyl groups (1715 cm^{-1}), as in the case of 1,3-indandione [9]. From this it follows that anhydrous 2-nitro-1,3-indandione exists in the nitrodiketo form (IV).

In the spectra of the dihydrate and the sodium salt of 2-nitro-1,3-indandione there were frequencies due to the mesomeric anion, the structure of which is close to the aci form (V); these frequencies were a characteristic frequency at 1640 cm^{-1} (somewhat low), the vibration frequency of the C = N bond of the aci form (1660 cm^{-1}) [10], and the frequencies due to the strong deformation vibrations of the C = O group (1660 and 1690 cm^{-1}). The band at 1620 cm^{-1} in the spectrum of the dihydrate was probably due to molecular vibration of the water molecule [11]. The frequency at 1350-1360 cm^{-1} can apparently be assigned to vibrations of the nitro group in the aci-form.

(IV)   (V)   (VI)
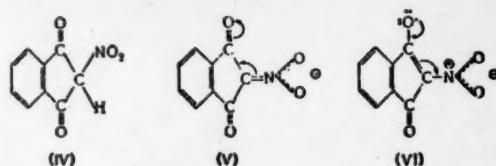
Thus, anhydrous 2-nitro-1,3-indandione and the dihydrate differ not only in water of crystallization, but are two compounds with different structures. The nitrodiketo form tends to transform to the ionic form (V-VI) not only when the anhydrous compound is dissolved in polar solvents, but also when the solid material is contacted with water vapor; the weak bands at 1641 and 1658 cm^{-1} indicate the existence of this form as an impurity in the anhydrous 2-nitro-1,3-indandione.

In the polarograms of aqueous solutions of 2-hydroxyimino-1,3-indandione and 2-nitro-1,3-indandione, the waves at the more negative potentials are due to reduction of the carbonyl groups of the indane ring (more accurately, of the corresponding anions). In the case of the 2-hydroxyimino-1,3-indandione, the first wave appeared in the region of highly positive potentials where reduction of the $-N=O$ group usually takes place $E_{1/2}$ for oximes is more negative by more than 1 volt). The nature of the first wave of the 2-nitro-1,3-indandione also indicates reduction of the nitro group rather than the aci form, since $E_{1/2}$ is close to the reduction potential of the nitro group in aliphatic nitro compounds (the aci form of nitroparaffins is not reduced at all at a dropping mercury electrode [12]).

The contradiction between the polarographic data, which seems to indicate the presence of nitroso and nitro groups in the compounds studied, and the i. r. spectroscopic data can be resolved if it is recalled that the development of a polarographic wave is associated with the entry of the molecule (or ion) into the electrode reaction. Since nitroso and nitro groups are reduced significantly more readily than hydroxyimino and aci-nitro groups,

respectively, the mesomeric anions, which can display dual reactivity, react as nitroso or nitro compounds at the electrode. The process which determines the electrode reaction is not a process which results in redistribution of the electron density of the anion, but is the process of diffusion of the anion to the electrode; therefore, the polarographic wave has the character of diffusion, not kinetic, waves.

These examples show that unequivocal conclusions as to the structure of compounds similar to those studied cannot always be formed from polarographic data.

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METHODS FOR THE PREPARATION OF TRIALLYLBORON
AND TRIVINYLBORON

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and A. A. Prokhorova

In recent years, a large number of papers has been published describing methods for the preparation and the properties of a whole series of new organoboron compounds. Papers on the synthesis of unsaturated boron compounds and their properties have appeared quite recently, and the scope of these papers is not exhaustive [1-3]. There is only a single publication, a patent disclosure, on the preparation of triallylboron [4]; according to this patent, triallylboron is obtained in a yield of 33% of theoretical by the interaction of triallyl borate with allylmagnesium bromide. Trivinylboron has been obtained as a mixture from vinylsodium and dimethylboron bromide [5, 6].

The present communication describes methods for the preparation of triallylboron from boron trifluoride and allylmagnesium bromide, boron trichloride and allylmagnesium bromide, and boron trifluoride and allylmagnesium chloride.

A method has recently been proposed for the preparation of vinylmagnesium bromide in tetrahydrofuran [6]. We have now applied this synthesis to the preparation of trivinylboron; this is the first time it has been so used. We prepared the compound in a medium of ether, and thereby were able to avoid decomposition of the vinylmagnesium bromide into ethylene and acetylene [7]. All experiments were carried out in nitrogen which had been carefully freed from oxygen.

EXPERIMENTAL

Interaction of boron trifluoride with allylmagnesium bromide. The experiments were carried out in an 0.5-liter four-necked flask fitted with a stirrer, a thermometer, a gas inlet tube for the introduction of nitrogen, and a reflux condenser; the reactants were charged to the flask in the following amounts: 48 g of magnesium, 60 g of allyl bromide, 37 g of boron trifluoride etherate, and 500 ml of absolute ether. After these materials had been charged to the flask, the reaction mixture was stirred for an additional hour. The ether was then distilled from the reaction mixture at atmospheric pressure on an oil bath (80-100°), following which a colorless, transparent, air-hypergolic fraction distilled; b. p. 62-65° (15 mm), yield 92%, d_4^{20} 0.7178, bromine number 340 (calculated 358.2), mol. wt. 134 and 136 (calculated 134).

$$\text{Found \%: C 80,16; H 11,39; B 8,45}$$
$$(CH_2 = CH - CH_2)_3B. \text{ Calculated \%: C 80,6; H 11,19; B 8,21}$$

Interaction of boron trifluoride with allylmagnesium chloride. 1.5 g (10% yield) of triallylboron (fraction with a b. p. of 62-65°) was obtained by the above-mentioned method from 23.8 g of magnesium turnings, 19 g of freshly distilled boron trifluoride etherate, and 50 g of allyl chloride in 300 ml of absolute ether.

$$\text{Found \%: C 80,70; H 11,50; B 7,80}$$
$$(CH_2 = CH - CH_2)_3B. \text{ Calculated \%: C 80,60; H 11,92; B 8,21}$$

Interaction of boron trichloride with allylmagnesium bromide. The experimental method and treatment of the reaction mixture was the same as described for the first experiment. From 24 g of magnesium turnings immersed in 250 ml of absolute ether, 80 g of allyl bromide, and 12.9 g of boron trichloride was obtained 1.49 g (10% yield) of triallylboron (fraction with a b. p. of 62-65°).

$$\text{Found \%: C 80,60; H 11,30; B 8,1}$$
$(CH_2 = CH - CH_2)_3B.$ Calculated %: C 80,60; H 11,19; B 8,21

The physicochemical properties were identical with those of the triallylboron obtained in the first experiment.

Interaction of boron trifluoride with vinylmagnesium bromide in a medium of tetrahydrofuran. To a four-necked flask, fitted with a reflux condenser, a stirrer, a funnel cooled with dry ice, and a gas inlet tube, were charged 12.15 g of magnesium turnings and 125 ml of dry tetrahydrofuran. The system was filled with nitrogen, a crystal of iodine was introduced to initiate the reaction, and 54.96 g of vinyl bromide was gradually added dropwise. The reaction took place very vigorously. The reaction mixture was heated at 80° for an hour. 22.3 g of a complex of boron trifluoride with tetrahydrofuran in 35 ml of tetrahydrofuran was added to the Grignard reagent. The reaction began immediately, and proceeded smoothly for 2 hours. At the conclusion of the reaction, the tetrahydrofuran was distilled from the reaction flask, and the tetrahydrofuran was followed by a liquid boiling in the range 75-85°; this latter fraction was a mixture of tetrahydrofuran and trivinylboron. It was not possible to separate the mixture by careful distillation. The trivinylboron was isolated in the form of the complex $(C_2H_3)_3B \cdot C_5H_5N$ by the action of pyridine on the mixture; the complex consisted of white crystals which deliquesced readily in air. B. p. 78-79°/6 mm, mol. wt. 172, 174 (calculated 171).

$$\text{Found \%: B 5,94; 6,02}$$
$(C_2H_3)_3B \cdot C_5H_5N.$ Calculated %: B 6,4

The boron analysis was carried out by the method proposed by B. M. Mikhailov and T. A. Shchegoleva [8]. The yield of trivinylboron was 67%.

When the tetrahydrofuran was replaced by other solvents (ether, vaseline oil, isopropylbenzene) after the preparation of the vinylmagnesium bromide, the yield of trivinylboron was decreased (the trivinylboron was again isolated as the pyridine complex).

Interaction of boron trifluoride with vinylmagnesium bromide in a medium of ether. 24 g of magnesium turnings and 250 ml of absolute ether were charged to the four-necked flask. Reaction was initiated with a crystal of iodine. A mixture consisting of 27 g of vinyl bromide and 36 g of boron trifluoride etherate was added dropwise from a dropping funnel cooled with dry ice. The reaction began immediately, and proceeded smoothly throughout the course of the experiment. The acetylene evolved was collected in an ammoniacal solution of cuprous chloride, and the ethylene was collected in bromine water. Upon completion of the reaction, the mixture was heated for 30 minutes at 75°. The ether was slowly distilled from the reaction flask, during which the bath temperature was maintained at not above 60°. The temperature was then gradually increased to 150°, thereby distilling a fraction which boiled at 79.5°; this was a colorless, transparent, hypergolic liquid with the odor characteristic of organoboron compounds. The yield was 70%, d_4^{20} 0.6812.

$$\text{Found \%: B 11,5; 10,98}$$
$(CH_2=CH)_3B.$ Calculated %: B 11,9

Thus, for the first time trivinylboron has been obtained as an individual compound, and, again for the first time, it has been synthesized in ether from vinylmagnesium bromide. The yield of acetylene and ethylene was insignificant.

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DIBENZOYLDIIMIDE (AZODIBENZOYL) IN THE DIENE SYNTHESIS

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Of the dienophiles with an active $-N=N$ bond, only derivatives of azodicarboxylic acid have as yet been used in the diene synthesis. The possibility of using in the diene synthesis dibenzoyldiimide, in which the $-N=N$ group is activated by two carbonyl groups, was studied in the present work.

The dibenzoyldiimide (I) was synthesized by oxidation of dibenzoylhydrazine with bromine (oxidation by chlorine has been described in the literature [1]):
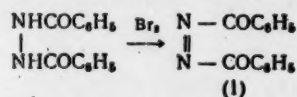
The diene synthesis was carried out in ether at room temperature. Addition products of dibenzoyldiimide with piperylene, 2,3-dimethylbutadiene, dicyclopentenyl, and phenylbutadiene were prepared in this manner. The yield of N,N'-dibenzoyl-Δ^4-tetrahydropyridazines (II) amounted to 70-80%.
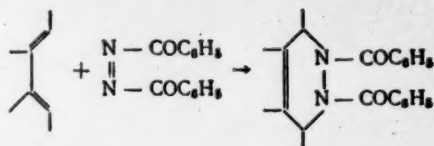
Attempts to introduce 1,4-diphenylbutadiene into the diene synthesis with dibenzoyldiimide were unsuccessful. This is explained by the low activity of 1,4-diphenylbutadiene (it is well known that with such active dienophiles as the diethyl ester of diazocarboxylic acid, it reacts at an appreciable rate only when heated [2]).

The structures of the addition products with piperylene and dicyclopentenyl were proved by showing that they were identical to the dibenzoyl derivatives of the corresponding Δ^4-tetrahydropyridazines (III) (which were obtained by hydrolysis of the addition products of the corresponding dienes with the diethyl ester of azodicarboxylic acid [3]), for example:
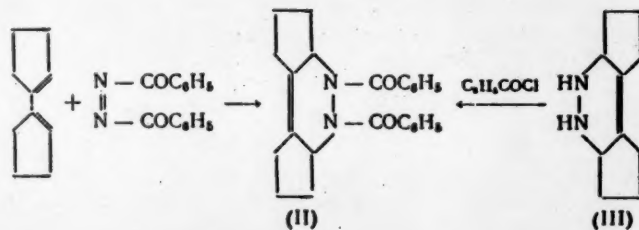
There was no depression of the melting point in mixed melting point tests. The partial hydrolysis product—N-benzoyl-3-phenyl-tetrahydropyridazine (V)—was obtained from the addition product (IV) of 1-phenylbutadiene with dibenzoyldiimide by heating with an equimolar amount of alcoholic alkali; this product differed in melting point from the monobenzoyltetrahydropyridazine (VII) prepared by benzoylation of 3-phenyl-Δ^2-tetrahydropyridazine (VI):

$$
\begin{array}{ccc}
\text{(VI)} & \xrightarrow{\ C_6H_5COCl\ } & \text{(VII)}
\end{array}
$$
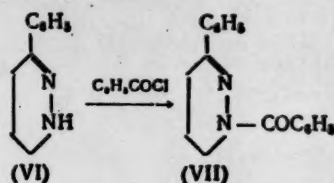
In this manner, it was shown that the benzoyl group farthest removed from the aromatic substituent is split off during partial hydrolysis of the dibenzoyl derivative of Δ^4-tetrahydropyridazine.

$$
\begin{array}{ccc}
\text{(IV)} & \xrightarrow{\ KOH\ } & \text{(V)}
\end{array}
$$
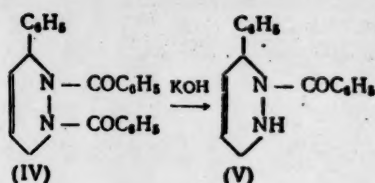
Upon further hydrolysis, our monobenzoyl derivative was converted to 3-phenyl-Δ^2-tetrahydropyridazine (VII) (which was also prepared by heating the original addition product with an excess of alkali); this compound was identified by its addition product with phenyl isothiocyanate:

$$
\begin{array}{ccccc}
\text{(V)} & \xrightarrow{\ KOH\ } & \text{(VI)} & \xrightarrow{\ C_6H_5NCS\ } &
\end{array}
$$
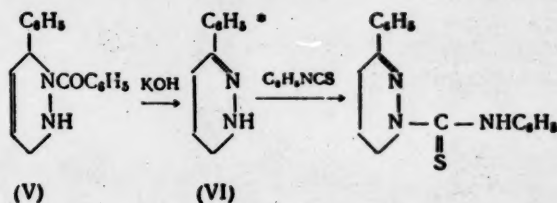
A mixture of this product with the derivative prepared from a known sample of 3-phenyl-Δ^2-tetrahydropyridazine melted without depression of the melting point.

It has thus been shown that dibenzoyldiimide is an active dienophile—it reacts in the cold with conjugated dienes forming N,N'-dibenzoyl-Δ^4-tetrahydropyridazines, the structure of which was demonstrated by alternate synthesis.

EXPERIMENTAL

Dibenzoyldiimide (azodibenzoyl). 60 g of dibenzoylhydrazine (prepared from benzoyl chloride and hydrazine hydrochloride [5]) was dissolved in 1.5 liters of a 0.22 N aqueous solution of NaOH; 0.5 liter of ether was added to the solution, and, with stirring, 88 g of bromine was introduced dropwise (at room temperature). After approximately one-third of the bromine had been added, simultaneous addition of a solution of 8.8 g of NaOH in 1 liter of H_2O was begun (the reagents were added over a period of 1.5-2 hours); the reaction mixture was then stirred for an additional hour. The ether layer was separated and washed with a solution of sodium thiosulfate; the crystalline mass remaining after distillation of the solvent was dibenzoyldiimide which was sufficiently pure for further use without additional purification: the yield was 25%; m.p. 119°; literature value [6]: m. p. 118°.

* Shifting of the double bond to the nitrogen during the course of a hydrolysis has been described for the case of addition products of the diethyl ester of azodicarboxylic acid with arylbutadienes [2, 4].

Diene synthesis. The addition products of dibenzoyldiimide and the various dienes were prepared by the usual method. A mixture of equimolar amounts (0.05 mole of each) of dibenzoyldiimide and the appropriate diene in 50 ml of ether was allowed to stand at room temperature for 6 hours. The ether was removed, and the resulting colorless, crystalline mass was recrystallized from alcohol.

1,2-Dibenzoyl-3-methyl-Δ^4-tetrahydropyridazine (from piperylene); the yield was 70%; m. p. 121-122°.

$$\begin{array}{llll} & \text{Found \%:} & \text{C } 74.58;\ 74.73; & \text{H } 6.21;\ 6.21; & \text{N } 9.07;\ 9.23 \\ \text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_2.\ \text{Calculated \%:} & \text{C } 74.49; & \text{H } 5.92; & \text{N } 9.14 \end{array}$$

1,2-Dibenzoyl-4,5-dimethyl-Δ^4-tetrahydropyridazine (from 2,3-dimethylbutadiene); the yield was 70%; m. p. 162-163°.

$$\begin{array}{llll} & \text{Found \%:} & \text{C } 74.71;\ 74.76; & \text{H } 6.11;\ 6.18; & \text{N } 8.77;\ 8.72 \\ \text{C}_{20}\text{H}_{20}\text{O}_2\text{N}_2.\ \text{Calculated \%:} & \text{C } 74.97; & \text{H } 6.29; & \text{N } 8.75 \end{array}$$

1,2-Dibenzoyl-3,4,5,6-biscyclopentano-Δ^4-tetrahydropyridazine (from dicyclopentenyl); the yield was 75%; m. p. 201-202°. A mixture with a known sample of dibenzoylbiscyclopentanotetrahydropyridazine (II) melted at 201-202° without depression ; literature value [3]: m. p. 202-202°.

1,2-Dibenzoyl-3-phenyl-Δ^4-tetrahydropyridazine (from phenylbutadiene); the yield was 80%; m.p. 143.5-144°.

$$\begin{array}{llll} & \text{Found \%:} & \text{C } 77.92;\ 78.01; & \text{H } 5.56;\ 5.47; & \text{N } 8.41;\ 8.45 \\ \text{C}_{24}\text{H}_{20}\text{O}_2\text{N}_2.\ \text{Calculated \%:} & \text{C } 78.24; & \text{H } 5.47; & \text{N } 8.69 \end{array}$$

Hydrolysis of 1,2-dibenzoyl-3-phenyl-Δ^4-tetrahydropyridazine (IV). Partial hydrolysis was carried out by heating for 6 hours equimolar amounts of the addition product and alkali (0.022 mole of each) in 40 ml of ethyl alcohol. The precipitated potassium benzoate was filtered; the alcoholic solution was allowed to stand, and the 2-benzoyl-3-phenyl-Δ^4-tetrahydropyridazine (V) crystallized out. The yield was 90%; m. p. 119-119.5°.

$$\begin{array}{llll} & \text{Found \%:} & \text{C } 77.25;\ 77.52; & \text{H } 6.12;\ 6.01; & \text{N } 10.28;\ 10.34 \\ \text{C}_{17}\text{H}_{16}\text{ON}_2.\ \text{Calculated \%:} & \text{C } 77.25; & \text{H } 6.10; & \text{N } 10.60 \end{array}$$

Complete hydrolysis was carried out under the same conditions as the partial hydrolysis, with the one exception that 0.66 mole KOH was used for the same amount of addition product (0.22* mole). After separation of the precipitated potassium benzoate, the reaction mixture was diluted with an equal volume of water and acidified with 2 N HCl to a neutral reaction. The hydrolysis product was extracted with ether, the ether extract was dried with magnesium sulfate, and after distillation of the solvent, the 3-phenyl-Δ^2-tetrahydropyridazine (VII) was distilled under vacuum; the yield was 85%; b.p. 165-166° (10 mm); literature value: b. p. 160° (8 mm) [2].

3-Phenyl-Δ^2-tetrahydropyridazine was also prepared from the partial hydrolysis product by heating the latter with an excess of alcoholic alkali for 6 hours. The addition product with phenyl isocyanate—3-phenyl-Δ^2-tetrahydropyridazine-1-thiocarboxanilide—melted at 106-108°; literature value [2]: m. p. 107-108°.

Benzoylation of 3-phenyl-Δ^2-tetrahydropyridazine was carried out by the method proposed for Δ^2-pyrazolines [7]. The yield of 1-benzoyl-3-phenyl-Δ^2-tetrahydropyridazine (VII) was 75%; m. p. 111.5-112°.

$$\begin{array}{llll} & \text{Found \%:} & \text{C } 77.12;\ 77.00; & \text{H } 6.14;\ 6.12; & \text{N } 10.59;\ 10.42 \\ \text{C}_{17}\text{H}_{16}\text{ON}_2.\ \text{Calculated \%:} & \text{C } 77.25; & \text{H } 6.10; & \text{N } 10.60 \end{array}$$

A mixture of VII with 2-benzoyl-3-phenyl-Δ^4-tetrahydropyridazine (V) melted with depression of the melting point (at 95-96°).

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IRREVERSIBLE CATALYSIS IN THE PRESENCE
OF METALLIC RHENIUM

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In previous communications [1-3] we have shown that metallic rhenium supported on activated carbon brings about the dehydrogenation of cyclic six-membered hydrocarbons and that the production of benzene from cyclohexane on a catalyst prepared from ammonium perrhenate (Re-1) is accompanied by the formation of small amounts of cyclohexene [3]; cyclohexene is not formed on a catalyst from the dioxane complex of rhenium heptoxide (Re-2). In order to ascertain the reason for the formation of cyclohexene on Re-1 and the ability of rhenium to cause irreversible catalysis (according to the terminology of N. D. Zelinskii), we have investigated the conversion of cyclohexene on both catalysts.
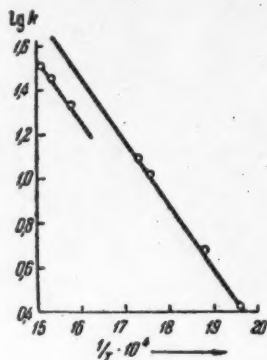
Fig. 1. Irreversible catalysis of cyclohexene on Re-1 catalyst.
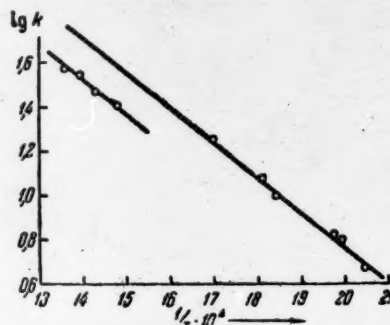
Fig. 2. Irreversible catalysis of cyclohexene on Re-2 catalyst.

The cyclohexene was prepared by the dehydration of cyclohexanol, and after purification had the following constants: b. p. 83°, n_D^{20} 1.4458, d_4^{20} 0.8102. Contact was accomplished by passing the cyclohexene over a layer of catalyst having a volume of 10 ml at the rate of 0.1 ml/min, and the temperature of the catalyst was measured with a chromel−copel thermocouple. The liquid reaction products (catalyzate) were collected in a cooled receiver and were analyzed for unsaturated hydrocarbons (cyclohexene) by means of the bromine number and for benzene by chromatography on silica gel in the presence of bisdiphenylenethylene [4]. The method of chromatographic analysis was somewhat modified and its applicability to our catalyzate was verified on control mixtures. The accuracy of the benzene determination was 0.5% absolute. The gaseous reaction products were collected in the gasometer of V. V. Patrikeev and according to the analysis consisted of hydrogen containing 6-8% of methane.

The conversion of cyclohexene in the presence of Re-1 and Re-2 was studied in the temperature range 215-465°. For both catalysts it was possible to clearly distinguish the temperature range where the process proceeded without the evolution of gas and where the relation $3C_6H_{10} = C_6H_6 + 2C_6H_{12}$ was maintained. Elevation of the reaction temperature led to the appearance of hydrogen.

The catalyzates from several experiments both on the Re-1 catalyst and on the Re-2 catalyst were combined, the unreacted cyclohexene was removed by methoxymercuration, and the mixture of benzene and cyclohexane obtained was separated by chromatography on silica gel. The benzene and cyclohexane were identified by their index of refraction and specific gravity. The constancy of activity of the catalysts was checked with respect to cyclohexane; repetition of several experiments with cyclohexene indicated good reproducibility.

The results of the individual experiments are given in Tables 1 and 2, where v is the rate of gas evolution in ml/min; k is the number of millimoles of benzene formed in 1 min on 1 ml of catalyst. In order to be able to compare the rate of formation of benzene from cyclohexane (cf. [1, 3]) and that from cyclohexene, we calculated the value $m = 3 \cdot 22.4 \cdot 10^6 k = 67.2 \cdot 10^6 k$, since in the case of the dehydration of cyclohexane we took for the rate constant the amount of hydrogen in milliliters that was evolved in 1 min on 1 ml of catalyst; in doing this we had to keep in mind that 3 moles of hydrogen were evolved for 1 mole of benzene. The relation of log k to the reciprocal of the temperature in the case of both Re-1 (Fig. 1) and Re-2 (Fig. 2) was represented by parallel straight lines. The energy of activation of the disproportionation of hydrogen in cyclohexene, calculated from the slope of the lines, was 12.8 kcal/mole for Re-1 and 7.7 kcal/mole for Re-2.

TABLE 1

Conversion of Cyclohexene, Rhenium Catalyst Re-1, $\epsilon = 12.8$ kcal/mole; $k_0 = 5.75 \cdot 10^4$

Temp., °C	Cyclohexene content of catalyzate, wt. %	$\frac{v}{}$ ml/min	$k \cdot 10^2$, mM/min·ml cat	m, ml/min·ml cat	m, calc.	lg k_0	$\frac{\epsilon}{\lg k_0} \cdot 10^{-4}$
248	92,0	0	0,26	0,175	0,18	4,74	2,70
259	85,5	0	0,48	0,32	0,32	4,76	2,69
297	68,1	0	1,05	0,71	0,69	4,77	2,68
306	61,8	0	1,23	0,83	0,83	4,76	2,69
				Average		4,76	2,69
362	40,0	1,3	2,17	1,46	1.46	4,56	2,81
380	30,3	3,7	2,85	1,91	1,91	4,56	2,81
392	26,2	5,6	3,27	2,20	2,24	4,55	2,82
				Average		4,56	2,81

In those experiments in which a considerable evolution of hydrogen was observed the reaction rate proved to be about $^2/_3$ that which would be expected from the extrapolated lines of Figs. 1 and 2. This could be explained by the fact that under the indicated conditions the process proceeds with a greater degree of conversion (60-75%) and here there is possible a deviation from the zero order. We note that N. A. Shcheglova and M. Ya. Kagan [5], who studied this reaction on platinum, determined that the disproportionation of hydrogen in cyclohexene goes according to the zero order.

Comparison* of the kinetic data for the dehydrogenation of cyclohexane and the disproportionation of hydrogen on Re-1 and Re-2 catalysts shows that the energy of activation of the two processes for the two catalysts coincide. Furthermore, the values of k_0 and ϵ /log k_0 are rather close. This indicates that both processes are limited, apparently, by the same stage. For the Re-2 catalyst the formation of benzene from cyclohexane goes

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*In making the comparison we must keep in mind that catalyst No. 9 in [2] and Re-1 of the present work are the same; Re-C in [1] and Re-2 are identical. The activity of the two catalysts toward cyclohexane in the series of experiments with cyclohexane and cyclohexene remained constant.

approximately twice as fast as from cyclohexene (Table 3). According to the data of M. Ya. Kagan and N. A. Shcheglova [6], the rate of dehydrogenation of cyclohexane on Pt is 1/4500 the rate of conversion of cyclohexene. M. Ya. Kagan and R. M. Flid [7] established that thermodynamically and kinetically (on Pd) the process of disproportionation of hydrogen goes more easily than the dehydrogenation of the hexamethylene hydrocarbons. From this information, the authors deduced the stepwise dehydrogenation of cyclic hydrocarbons. The mechanism employed by them can be represented by the following scheme:

$$3C_6H_{12} \xrightarrow{m_2} 3C_6H_{10} + 3H_2$$
$$3C_nH_{1n} \xrightarrow{m_2} C_6H_6 + 2C_6H_{12}$$
$$\overline{C_6H_{12} \xrightarrow{m_1} C_6H_6 + 3H_2}$$
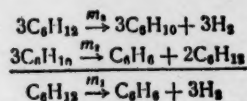
TABLE 2

Conversion of Cyclohexene, Rhenium Catalyst Re-2, ϵ = 7700 cal/mole, k = 8.9·10²

Temp., °C	Anal. of catalyzate wt. -%		v, ml/min	k·10², mM/min ·ml cat.	m, ml/min·ml cat.	m, calc.	lg k_0	$\frac{\epsilon}{\lg k_0}$·10⁻⁶
	C_6H_{12}	C_6H_6						
215	85,8	5,18	0	0,47	0,32	0,32	2,95	2,61
229	80,8	6,90	0	0,63	0,42	0,40	2,97	2,60
233	80,0	—	0	0,66	0,44	0,43	2,96	2,60
270	69,1	—	0	1,02	0,69	0,71	2,94	2,62
279	63,8	10,8	0	1,19	0,80	0,81	2,94	2,62
316	45,2	19,1	1,4	1,81	1,21	1,26	2,93	2,63
						Average	2,95	2,61
404	39,9	—	3,9	2,51	1,72	1,66	2,71	2,84
427	38,0	39,0	5,9	2,93	1,97	2,00	2,69	2,86
445	34,0	43,5	9,0	3,52	2,39	2,30	2,71	2,84
464	34,0	44,5	9,9	3,65	2,45	2,53	2,67	2,88
						Average	2,70	2,86

Here we are omitting the stage of formation of cyclohexadiene in order not to complicate the scheme and the reasoning.

On the other hand, on the basis of the principle of structural conformity of the multiplex theory [8] both for the catalysts considered by M. Ya. Kagan et al., (Pt, Pd) and for rhenium, we would expect a sextet mechanism of dehydrogenation, i. e., a process proceeding without intermediate stages, with the simultaneous splitting out of three molecules of hydrogen.

It is not difficult to see that if the stepwise mechanism were correct, then $m_1 \leq m_2$. This necessary (although not sufficient) condition is fulfilled in the work reported in [6]. According to the experimental data of the present work, on the contrary, $m_1 > m_2$. Thus, the results obtained indicate that the dehydrogenation of cyclohexane on rhenium proceeds not by a stepwise mechanism, but by a sextet mechanism.

On the Re-1 catalyst the rate of formation of benzene from cyclohexene was greater than from cyclohexane, being about twice the latter (Table 4). Although for the Re-1 catalyst $m_1 < m_2$, it is difficult to suppose that on catalysts of the same chemical nature and on the same carrier the dehydrogenation of cyclohexane proceeds by a different mechanism. Here we should note that cyclohexene is formed on the Re-1 catalyst, in spite of the fact that the rate of conversion of cyclohexene is 6-8 times greater than that of cyclohexane.

If cyclohexene were the main intermediate product (as follows from the above scheme), then with the ratio of rates of conversion of cyclohexene and cyclohexane that occurs on the Re-2 catalyst cyclohexene should be detected in the catalyzate. However, as shown above, cyclohexene was not detected on Re-2. Thus, cyclohexene,

TABLE 3

Rhenium Catalyst Re-2; $(\epsilon/\log k_{01}) \cdot 10^{-3} = 2.42$; $(\epsilon/\log k_{02}) \cdot 10^{-3} = 2.61$

Temp., °C	Rate of formation of benzene from		$n°$
	cyclohexane, $k_{01} = 1.7 \cdot 10^2$	cyclohexene $k_{02} = 8.9 \cdot 10^2$	
246	0.98	0.46	1.40
272	1.35	0.63	1.98
281	1.49	1.00	1.22
284	1.50	1.02	2.32
341	2.70	1.82	4.04

•$\underline{n}$ is the number of moles of cyclohexene converted in 1 min on 1 ml of catalyst multiplied by $67.2 \cdot 10^9$.

TABLE 4

Rhenium Catalyst Re-1; $(\epsilon/\log k_{01}) \cdot 10^{-3} = 2.96$; $(\epsilon/\log k_{02}) \cdot 10^{-3} = 2.69$

Temp., °C	Rate of formation of benzene from		n
	cyclohexane, $k_1 = 2.11 \cdot 10^4$	cyclohexene, $k_{02} = 5.75 \cdot 10^4$	
301	0.28	0.74	2.22
360	0.78	1.37	4.12
398	1.31	2.50	6.84
413	1.84	3.08	9.25

which is formed in amounts of 1-1.5% in the dehydrogenation of cyclohexane on Re-1, is not the main intermediate product, but is obtained as a result of a side dehydrogenation that takes place to a small extent along with the sextet mechanism.

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POLYMERIZATION OF 3-METHYLBUTENE-1

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The stereoregular polyolefins produced by the polymerization of some slightly branched α-olefins with complex organometallic catalysts are characterized by a high melting point, which favorably distinguishes them from a number of similar polymers. The investigation of the polymerization of branched α-olefins to produce stereoregular polymers and the study of the properties of the latter are of substantial theoretical interest in the solution of the general problem of establishing the relationship between the reactivity of the monomers and the structure and properties of the stereoregular polyolefins. In this connection we undertook the investigation of the polymerization of 3-methylbutene-1 with complex organometallic catalysts.

EXPERIMENTAL

The starting monomer, 3-methylbutene-1, was prepared by pyrolysis of isoamyl acetate having the following constants: n_D^{21} 1.4003 (lit. n_D^{21} 1.3999), d_4^{15} 0.8766 (lit. d_4^{15} 0.8762), b. p. 136.5-139.5° (lit. b. p. 142°).

A preliminary investigation of the pyrolysis limits showed that the greatest content of the desired hydrocarbon in the products of pyrolysis of the acetate was obtained at a temperature of 600° and a volume velocity (in the gas phase) of 180 hour^{-1}.
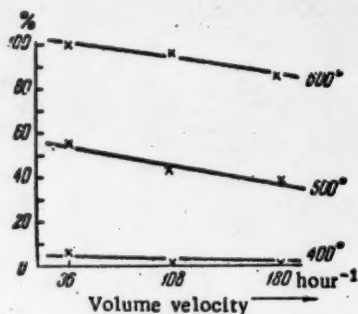
Fig. 1. Relation of percent breakdown of isoamyl acetate to volume velocity and temperature.
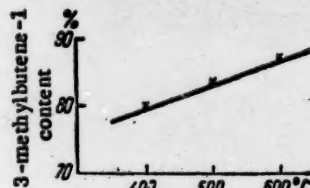
Fig. 2. Relation of 3-methylbutene-1 content of gas to breakdown temperature at a feed volume velocity of isoamyl acetate of 36 hour^{-1}.

Under these conditions the degree of breakdown of the acetate was 84-89% and the 3-methylbutene-1 content of the gases was 97% (analysis by gas–liquid chromatography). The relationships observed in the pyrolysis of isoamyl acetate are represented graphically in Figs. 1 and 2. The 3-methylbutene-1 formed on pyrolysis of the isoamyl acetate was condensed in chilled traps, dried over calcium hydride, and then distilled over metallic sodium on a filled column with a fractionating power equivalent to 60 theoretical plates. The product thus obtained had the following constants:

	B. p. °C at 760 mm Hg	n_D^{20}
Found	19.0-21.0	1.3645
Literature data	29.1	1.3640

Al(C_2H_5)$_3$ or Al(i-C_4H_9)$_3$ and TiCl$_4$ or TiCl$_3$ were employed as catalyst components. The aluminum alkyls were used in benzine solution and according to analysis contained Al(C_2H_5)$_3$ 0.3 g/ml and Al(i-C_4H_9)$_3$ 0.32 g/ml. The titanium trichloride was prepared by reduction with metallic sodium and contained 65% TiCl$_3$ and 35% NaCl.

The polymerization of 3-methylbutene-1 was carried out in rotating sealed ampoules (v = 35 ml) placed in a thermostat. Heptane that had been carefully purified and dried by distillation over metallic sodium was used as the solvent. The ampoule was previously flushed out with oxygen-free argon and the polymerization was carried out under argon. The starting components and the catalyst also were loaded into the cooled ampoule in a current of purified argon.

At the end of the experiment the ampoule was opened and the contents were treated with acidified methanol to decompose the remaining catalyst. The solid polymer formed in the polymerization was filtered off, washed consecutively with methanol and water, and then dried in vacuo to constant weight. In case of polymerization on TiCl$_3$, the polymer was carefully washed with hot water to free it of NaCl. The poly-3-methylbutene-1 thus obtained was a white powder with m. p. about 240°. The characteristic viscosity of the polymer in tetralin (under nitrogen) at 135° (preliminary solution of the polymer in tetralin was carried out at 180°) was determined, and also the amount of the isotactic fraction consecutively extracted with boiling ether and heptane, as in the investigation of polypropylene. Some samples were subjected to x-ray study (cf. Fig. 3). We cite here the most characteristic experiments:

Experiment 10. Catalyst Al(C_2H_5)$_3$ + TiCl$_4$ in the ratio 1.6 : 1. Total concentration of catalyst in reaction medium (monomer and solvent) 5% by weight. Polymerization temperature 20°, duration of experiment 2 hours. M. p. of polymer 240°, characteristic viscosity 0.44. Content of fraction soluble in boiling ether 26.3%; soluble in boiling heptane 24.3%; insoluble in boiling heptane 49.4%.

Experiment 27. Catalyst Al(i-C_4H_9)$_3$ + TiCl$_3$ in the ratio 0.8 : 1. Total concentration of catalyst 2.8%. Polymerization temperature 70°, time of experiment 25 hours. M. p. of polymer 210°; characteristic viscosity 0.15; content of fraction soluble in boiling ether 11%; soluble in boiling heptane 58%; insoluble in boiling heptane 31%.
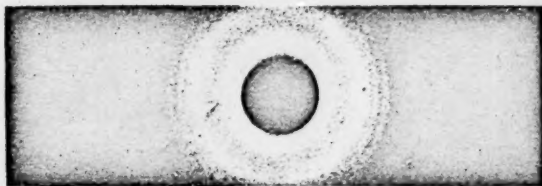
Fig. 3. X-ray pattern of isotactic fraction of poly-3-methyl-butene-1.

The small content of isotactic fraction in this case is explained by the use of triisobutyl aluminum instead of triethyl aluminum, and also by the disturbance of the surface of the TiCl$_3$ by the presence of sodium chloride on it in considerable amounts.

SALTS OF FLUOROOXYMOLYBDIC ACIDS

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Investigation of the system $HF-MoF_6-H_2O$ by the isothermal solubility method [1] has shown that hydrolysis of molybdenum hexafluoride is accompanied by the formation of the fluorooxymolybdic acids $H_2MoO_3F_2 \cdot H_2O$. and $H_2MoO_2F_4 \cdot 1.5H_2O$. These materials, representatives of a new class of chemical compounds of molybdenum, were studied in the solid form [1, 2] and in solution [3].
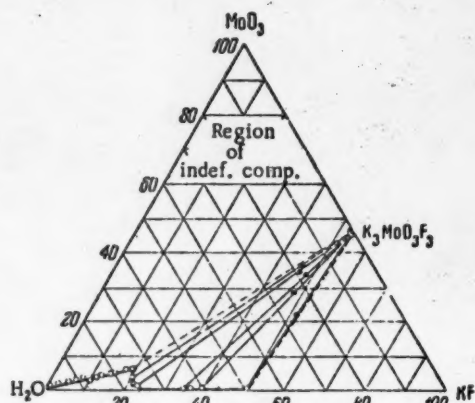
Fig. 1. Solubility isotherm of the system $KF-MoO_3-H_2O$ (25°).

Starting with the fact of the existence of such acids, it was of interest to establish the correspondence between these acids and their salts. For this purpose we studied the system $KF-MoO_3-H_2O$ by the isothermal solubility method (isotherm 25°). Investigation of this system was carried out in a similar manner to that of the system $HF-MoF_6(MoO_3)-H_2O$ [1], with the replacement of hydrofluoric acid by potassium fluoride. The data obtained permit the following conclusions (cf. Fig. 1):

1. With an increase in the concentration of potassium fluoride in the solution, the solubility of molybdenum trioxide increases, reaching a maximum at a KF concentration of 19.0%.

2. The initial concentrations of potassium fluoride in the system show regions of solid phases of variable composition. This fact indicates the possibility of the formation of solid solutions in this region.

3. An increase in the potassium fluoride concentration in the solution ($KF > 19.0\%$) leads to a sharp decrease in the solubility of molybdenum trioxide. The composition of the solid phase in this portion of the solubility curve remains constant and corresponds to the compound $K_3MoO_3F_3$. This solid phase was isolated and subjected to chemical analysis, which confirmed the composition obtained by the graphic method of Shreinemakers.

$$
\begin{array}{ll}
\text{Found} & \text{\%: } MoO_3\ 44.89;\ KF\ 54.92 \\
K_3MoO_3F_3. \text{Calculated} & \text{\%: } MoO_3\ 45.23;\ KF\ 54.77. \\
\text{Ratio} & KF:MoO_3 = 3.03:1
\end{array}
$$

4. As has been shown previously by the authors [2], the water in the difluorooxymolybdic acid enters into
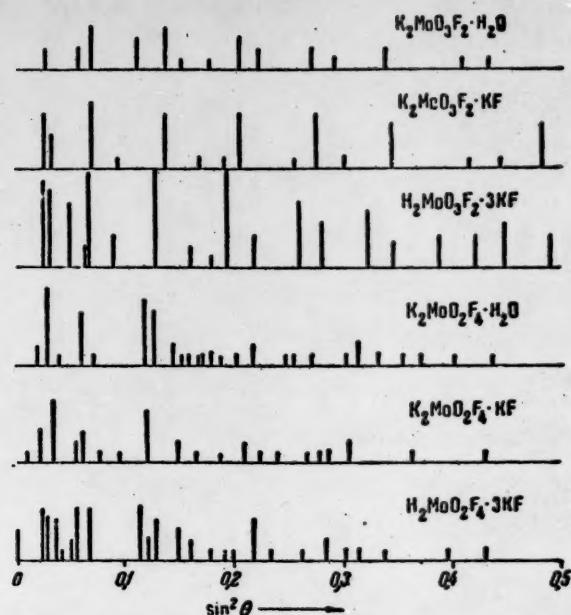
Fig. 2. X-ray patterns of potassium salts of fluorooxy-
molybdic acids.

the internal sphere of the complex compound. This fact provides a basis for the assumption of the known connection with respect to structural characteristics between difluorooxymolybdic acid $H_2MoO_3F_2 \cdot H_2O$ and the phase separating out in the system $KF-MoO_3-H_2O$ ($K_2MoO_3F_2 \cdot KF$), which appears as the potassium salt of difluorooxymolybdic acid. In a study of the behavior of an aqueous solution of molybdenum trioxide and potassium fluoride, Schmitz-Dumont and Opgenhoff [4] isolated a series of compounds that it is now possible to identify as salts of fluorooxymolybdic acids. It is interesting, however, to note that when these authors reacted molybdenum trioxide directly with excess aqueous potassium fluoride solution [4] they obtained only the compound corresponding to the solid phase that separates out in the system $KF-MoO_3-H_2O$, i. e., $K_3MoO_3F_3$. All the other compounds were obtained under less specific conditions. On our part we undertook an investigation of the precipitates formed in the reaction of aqueous solutions of the fluorooxymolybdic acids with potassium fluoride and with potassium hydroxide, the latter in the course of neutralization and formation of KF in the solutions under investigation. Both processes corresponded to the separation of precipitates at some of the extreme points of the more complex system $HF-MoO_3-KF-H_2O$.

Besides the solutions corresponding to the compositions of the fluorooxymolybdic acids (F : Mo = 4 and 2), we used solutions with an excess of hydrogen fluoride (F : Mo > 4) and also aqueous solutions (F : Mo = 0). The precipitates obtained were filtered, dried at 60-70°, and subjected to chemical analysis (cf. Table 1). As can be seen from the table, in the example taken it proved to be possible to synthesize a series of potassium salts of fluorooxymolybdic acids.

Besides the modes of synthesis given, we used a method in our work based on the hydrolysis of the compounds $H_2MoO_2F_4 \cdot 3KF$ and $K_2MoO_2F_4 \cdot KF$, obtained under the conditions of the system $HF-MoO_3-KF-H_2O$ (cf. Table 1). When the compounds mentioned were recrystallized, they underwent partial hydrolysis according to the equation (cf. Table 1):

$$H_2MoO_2F_4 \cdot 3KF + H_2O = K_2MoO_2F_4 \cdot H_2O + KF + 2HF,$$

$$K_2MoO_2F_4 \cdot KF + H_2O = K_2MoO_2F_4 \cdot H_2O + KF.$$
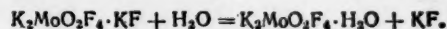
In this way we demonstrated the formation of the potassium salt of tetrafluorooxymolybdic acid upon hydrolysis of compounds containing larger amounts of fluorine.

All of the salts isolated were subjected to x-ray study. The data from the x-ray analysis showed (Fig. 2) the individuality of the compounds obtained. The x-ray patterns for the potassium salts of any one acid are of almost the same type and differ distinctly from the same kind of salts of different acids. Comparison of the x-ray patterns obtained with those of some salts previously isolated by Schmitz-Dumont and Opgenhoff [4] by the procedure shown below:

$$MoO_3 + nKF + aq \begin{cases} \xrightarrow[98°]{n>6} K_3MoO_3F_3 \rightarrow \text{ filtrate } \rightarrow K_2MoO_3F_2 \cdot H_2O \\[2pt] \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \\[2pt] \qquad\qquad\qquad\qquad\qquad\qquad K_2MoO_3F_2 \\[2pt] \qquad\qquad\qquad\qquad\qquad\qquad \text{(unstable)} \\[6pt] \xrightarrow[25°]{n<6} K_3Mo_4O_{13}F \cdot 3H_2O \xrightarrow[-3H_2O]{110°} K_3Mo_4O_{13}F \\[2pt] \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(unstable)} \\[2pt] \qquad\quad \hookrightarrow \text{ filtrate } \rightarrow K_2MoO_2F_4 \cdot H_2O \\[6pt] \xrightarrow[98°]{n=0.5} K_2Mo_4O_{13} \end{cases}$$
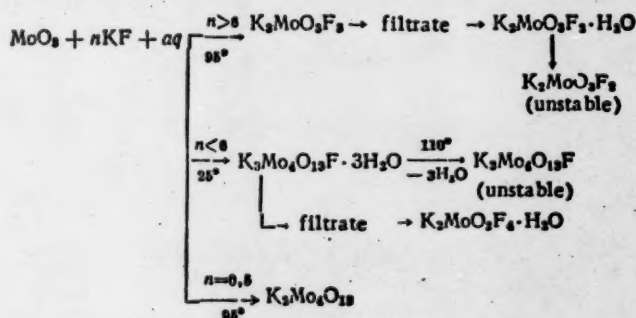
showed that in both instances the same compounds were obtained (cf. Fig. 3). Some divergence in the x-ray patterns is observed for the salt $K_2MoO_3F_2 \cdot H_2O$ in comparison with the literature data. These deviations can be explained by the fact that Schmitz-Dumont and Opgenhoff [4] had a different phase because they used a method of preparation different from ours.
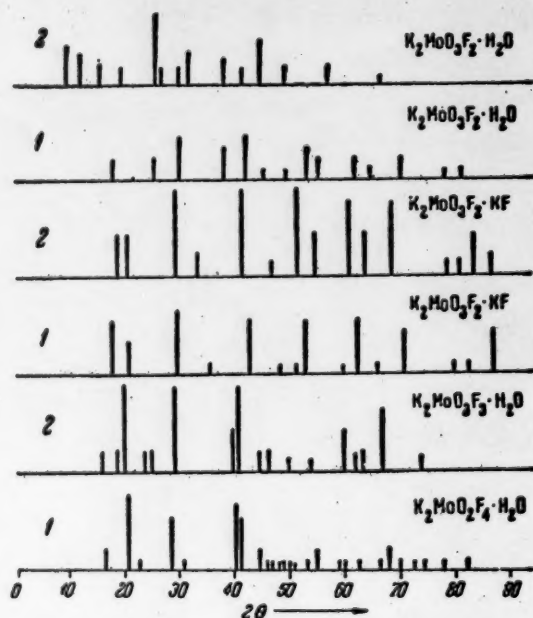
Fig. 3. X-ray patterns of potassium salts of fluorooxymolybdic acids (1—author's data, 2—data from [4]).

Thus, the phases obtained were identified with those known in the literature and agreed with the results of chemical analysis. The fact of the existence of these salts [1, 2, 3] also favors the formulas given.

The compounds can be arranged in a series according to the amount of fluorine in the molecule: $K_2MoO_4 \rightarrow K_2MoO_3F_2 \cdot H_2O \rightarrow K_2MoO_3F_2 \cdot KF \rightarrow K_2MoO_2F_4 \cdot H_2O \rightarrow H_2MoO_3F_2 \cdot 3KF \rightarrow K_2MoO_2F_4 \cdot KF \rightarrow H_2MoO_2F_4 \cdot 3KF$.

TABLE 1

Chemical Analysis of Salts

Composition of starting solution in %	F	Mo	F : Mo	Composition
	In percent			
System HF−MoO₃−KF−H₂O				
Aqueous solution H₂MoO₄	17,91 / 18,65	30,15 / 29,40	3,00 / 3,21	$K_3MoO_3F_3$
MoO₃ 27,45; HF 8,08 F : Mo = 2,12	26,78 / 26,28	26,52 / 26,07	5,00 / 5,08	$H_3MoO_3F_3 \cdot 3KF$
MoO₃ 26,75 HF 15,96 F : Mo = 4,29	34,98 / 34,68	25,23 / 25,46	7,00 / 6,89	$H_2MoO_2F_6 \cdot 3KF$
MoO₃ 22,60 HF 23,35 F : Mo = 7,53	27,92 / 28,38	28,20 / 28,05	5,00 / 5,12	$K_2MoO_2F_4 \cdot KF$
System HF−MoO₃−KOH−H₂O				
MoO₃ 20,15 HF 11,12 F : Mo = 2,00	13,60 / 14,54	34,42 / 32,21	2,00 / 2,27	$K_2MoO_3F_2 \cdot H_2O$
MoO₃ 25,10 HF 13,64 F : Mo = 3,91	17,91 / 18,19	30,15 / 31,07	3,00 / 2,95	$K_3MoO_3F_3$
MoO₃ 28,89 HF 24,34 F : Mo = 6,05	17,91 / 18,68	30,15 / 31,43	3,00 / 3,00	$K_3MoO_3F_3$
Salts obtained by hydrolysis				
Aqueous solution H₂MoO₂F₄ · 3KF	25,32 / 25,76	31,97 / 31,85	4,00 / 4,08	$K_3MoO_3F_4 \cdot H_2O$
Aqueous solution K₂MoO₂F₄ · KF	25,32 / 25,65	31,97 / 31,60	4,00 / 4,10	$K_2MoO_3F_4 \cdot H_2O$

Note: Figures above line are calculated, those below line are found.

The salts isolated correspond to the acids previously isolated in the system $HF-MoF_6(MoO_3)-H_2O$ [1]. The formation of the acids is connected with hydrolysis in the series: $MoF_6 \rightarrow H_2MoO_3F_2 \cdot H_2O \rightarrow H_2MoO_2F_4 \rightarrow H_2MoO_4$.

The acids themselves should be highly hydrolyzed in dilute solutions and an attempt to obtain the salts from such solutions by neutralizing them with alkali did not give positive results, since complete hydrolytic breakdown of the starting acid takes place. For this reason, we used for the synthesis of the salts of the fluorooxymolybdic acids the methods indicated above, based on a study of the precipitates isolated at the extreme points of the system $HF-MoO_3-KF-H_2O$.

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REACTION OF TRIETHYLSILANE WITH SECONDARY
AND TERTIARY VINYLETHYNYLCARBINOLS IN THE PRESENCE
OF H_2PtCl_6

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A great deal of work has been devoted to the action of various hydrosilanes on unsaturated compounds in the presence of catalysts. The usual catalysts are ultraviolet rays, peroxides, $AlCl_3$, $AlBr_3$, $ZnCl_2$, BCl_3, and others. But some of these catalysts, for example peroxides and ultraviolet rays, give low yields of the addition products in the case of high molecular olefins, or do not catalyze the reaction at all. In 1954 Wagner et al. [1] successfully used platinized carbon in addition reactions of hydrosilanes and olefins. These authors showed that in the case of platinized carbon polymerizing side reactions take place to a smaller extent and the yields are higher.

A. D. Petrov, V. A. Ponomarenko, et al. [2], in an investigation of the addition of hydrosilanes to unsaturated compounds in the presence of Pt/C, used methyldichlorosilane and ethyldichlorosilane and showed that while these hydrosilanes with allyl chloride and a metal chloride give low yields when peroxides and ultraviolet rays are used, the yields of α-chloroalkylalkyldichlorosilanes are increased in the case of Pt/C, but here also there is a polymerization side reaction.

Continuing the work in this direction, A. D. Petrov et al. [3] investigated other metals of the eighth group on various carriers for the abovementioned reactions. The catalysts studied were divided into two groups: catalysts that promoted the main reaction and those that promoted the side reaction.

Recently, work has been published by Speier et al. [4], who proposed a new catalyst, 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. It appeared that this catalyst had a higher activity and made it possible to carry out the addition of the hydrosilanes to olefins at room temperature, at the same time decreasing the reaction period and increasing the yield of the addition products. In our work described in [5] we investigated the reaction of triethylsilane with vinylethynylcarbinols in the presence of Pt/C, and in the present investigation we repeated the reaction using 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol for the purpose of increasing the yields of addition products and simplifying the reaction conditions. As we have shown previously, the reaction of triethylsilane with vinylethynylcarbinols takes place according to the following scheme:

$$\begin{matrix} R \\ | \\ C \\ | \\ R \end{matrix} - C \equiv C - CH = CH_2 + (C_2H_5)_3 SiH \xrightarrow[Pt/C]{} \begin{matrix} R & OH \\ | & | \\ C - C = CH - CH = CH_2 \\ | & | \\ R & Si(C_2H_5)_3 \end{matrix} \qquad (I)$$
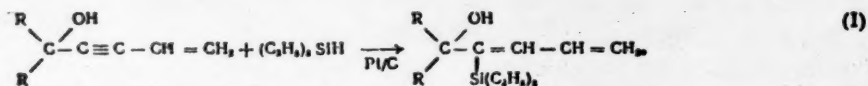
and the yields of addition products vary from 25 to 52% of theoretical.

It appeared that when $H_2PtCl_6 \cdot 6H_2O$ is used, the reaction goes at room temperature and is completed in 2 hours and the yields in the case of tertiary vinylethynylcarbinols are considerably increased, reaching 55-65% of theoretical. However, with secondary carbinols the reaction goes differently with the formation of an ether:

$$ (II) $$

$$RCHOH - C \equiv C - CH = CH_2 + (C_2H_5)_3 SiH \cdot \overset{OSi(C_2H_5)_3}{RCH} - C \equiv C - CH = CH_2$$
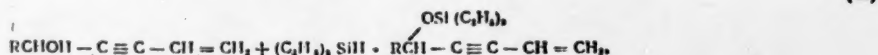
In 1953 A. D. Petrov and co-workers [6] suggested that the reaction of a Grignard reagent with an acetylenic alcohol, and then with R_3SiX may proceed according to both equation (a)

$$\underset{CH_3}{\overset{CH_3}{C}} - C \equiv CMgX + R_3SiX \rightarrow \underset{CH_3}{\overset{CH_3}{C}} - C \equiv CH, \qquad (a)$$

and equation (b)
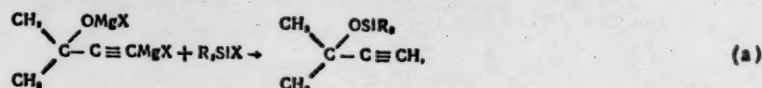
$$\underset{CH_3}{\overset{CH_3}{C}} - C \equiv CMgX + R_3SiX \rightarrow \underset{CH_3}{\overset{CH_3}{C}} - C \equiv SiR_3. \qquad (b)$$
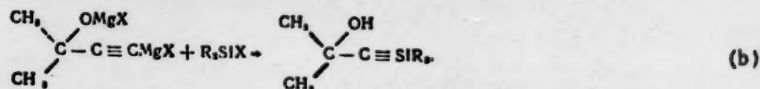
But later on, both the authors [7] and I. A. Shikhiev [8, 9] and co-workers demonstrated that the reaction under the conditions studied goes only according to equation (b). In our case it appeared that the reaction may follow scheme I or scheme II depending on the conditions, the nature of the carbinol, and the catalyst.

To identify the organosilicon ether obtained, we carried out the counterpart reaction:

$$RCHOH - C \equiv C - CH = CH_2 + (C_2H_5)_3 SiCl \rightarrow \underset{\overset{|}{OSi(C_2H_5)_3}}{RCH} - C \equiv C - CH = CH_2. \qquad (III)$$
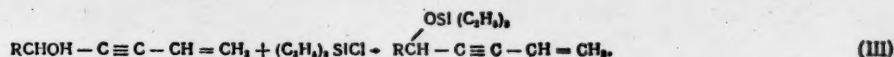
All the constants of the compound $\left(R - \underset{\overset{|}{OSi(C_2H_5)_3}}{CH} - C \equiv C - CH = CH_2 \right)$, obtained by both scheme II and scheme III agreed

well. Thus, it can be affirmed that the addition of hydrosilanes to secondary vinylethynyl alcohols goes according to schemes I and II. This depends on the character of the catalyst and the unsaturated starting compound.

TABLE 1

Compound obtained	Yield, % of theo.	B. p. °C/mm	n_D^{20}	n_4^{20}	MR_D	
					found	calc.
$CH_2=C-C-CH-CH=CH_2$ $\quad\ CH_3Si(C_2H_5)_3$	60,8	78°/3 mm	1,4850	0,8381	71,11	70,54
$CH_3-CH=C-C=CH-CH=CH_2$ $\quad\quad CH_3Si(C_2H_5)_3$	89,0	89°/3 mm	1,4865	0,8417	75,77	75,17
$\langle\ \rangle C-C=CH-CH=CH_2$ $\quad\ Si(C_2H_5)_3$	28,6	106°/3 mm	1,5048	0,9014	81,57	82,30
$OSi(C_2H_5)_3$ $CH_3-CH-C\equiv C-CH=CH_2$ $\quad\ O Si(C_2H_5)_3$	15,2	94–95°/5 mm	1,4560	0,8596	66,40	66,00
$n\text{-}C_3H_7CH-C\equiv C-CH=CH_2$	10,7	90–92°/2 mm	1,4592	0,8625	75,45	75,26

We also carried out the dehydration with $KHSO_4$ of the organosilicon compounds obtained that had double bonds in the α- and γ-position to the silicon atom and a hydroxyl group in the β-position. The dehydration went smoothly and trienes were obtained in good yields according to the scheme:

$$\underset{R}{\overset{R'}{C}} - \underset{Si(C_2H_5)_3}{\overset{OH}{C}} = CH - CH = CH_2 \xrightarrow[KHSO_4]{-H_2O} \underset{R}{RCH} = C - \underset{Si(C_2H_5)_3}{C} = CH - CH = CH_2.$$
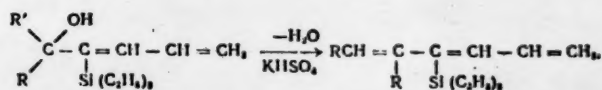
The trienes obtained were colorless, mobile liquids that turned yellow on standing and polymerized. The secondary organosilicon alcohols obtained over Pt/C were not dehydrated under these conditions. The properties of the trienes, which were prepared for the first time, and of the organosilicon ethers are given in Table 1.

EXPERIMENTAL

Action of triethylsilane on dimethylvinylethynylcarbinol. In a three-necked flask were placed 27.5 g of the carbinol, 29 g of triethylsilane, and 2 ml of 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. Stirring was continued until the mixture cooled to room temperature (approximately 2 hours), after which it was distilled in vacuo under nitrogen. The following fractions were obtained: I with b. p. 34-35°/3, 8.7 g; II with b. p. 78-81°/2, 31 g; remainder polymerized. Fraction II had n_D^{20} 1.4867; d_4^{20} 0.8903; found MR_D 72.95; OH 7.29 and 7.63%; calculated MR_D 72.56; OH 7.57%; yield 54.9% of theoretical .

$$\text{Found \%: C 69,06; 69,24; H 11,54; 11,71; Si 12,25; 11,72}$$
$$C_{13}H_{26}OSi: \text{ Calculated \%: C 69,02; H 11,50; Si 12,38.}$$

Dehydration of $C_{13}H_{26}OSi$. 5 g of compound, 2 g of $KHSO_4$ (fused), and 0.1 g of dithizone were used; they were placed in an apparatus for vacuum distillation and the mixture was heated to a temperature of not more than 100° under nitrogen for 40 min, after which it was distilled; 2.8 g of a fraction with b. p. 78°/3 was obtained; yield 60.8% (of theoretical); found n_D^{20} 1.4850; d_4^{20} 0.8381; MR_D 71.11; calculated 70.54.

$$\text{Found \%: C 75,33; 75,21; H 11,86; 11,60; Si 13,13; 13,28}$$
$$C_{13}H_{24}Si. \text{ Calculated \%: C 75,00; H 11,53; Si 13,46.}$$

Action of triethylsilane on methylethylvinylethynylcarbinol. Under similar conditions, 31 g of the carbinol, 29 g of triethylsilane, and 3 ml of 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol were used. After distillation the following fractions were obtained: I, 40-57°/7, 2 g; II, 57°/7, 2 g; III, 80-100°/3, 6 g; IV, 108-110°/3, 39 g; the remainder polymerized. Fraction IV had n_D^{20} 1.4889; d_4^{20} 0.8942; yield 65% of theoretical ; found MR_D 77.45; calculated 77.19; OH 7.13 and 6.76% calculated OH 7.12%.

$$\text{Found \%: C 69,99; 70,12; H 11,69; 11,90; Si 11,43; 11,61}$$
$$C_{14}H_{28}OSi. \text{ Calculated \%: C 70,00; H 11,66; Si 11,66.}$$

Dehydration of $C_{14}H_{28}OSi$. 3 g of compound, 2 g of $KHSO_4$, and 0.2 g of dithizone were used; after 40 min boiling the mixture was distilled under nitrogen; 2.4 g of a fraction was obtained with b. p. 89°/3, yield 2.4 g or 89% of theoretical ; found n_D^{20} 1.4865; d_4^{20} 0.8417; MR_D 75.77; calculated 75.17.

$$\text{Found \%: C 75,54; 75,60; H 11,92; 11,88; Si 12,15; 12,20}$$
$$C_{14}H_{26}Si. \text{ Calculated \%: C 75,67; H 11,71; Si 12,61.}$$

Action of triethylsilane on methylvinylethynylcarbinol. 24 g of the carbinol, 29 g of triethylsilane, and 2 ml of 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol were used. After distillation the following fractions were obtained: I, b. p. 37°/2, 5 g; II, b. p. 69-71°/2, 2.5 g; III, b. p. 72-74°/2, 1.2 g; IV, b. p. 79-80°/3, 5.5 g; V, b. p. 94-95°/5, 8 g; VI, b. p. 59-60°/7, 5 g; VII, b. p. 125-126°/2, 7 g. Fraction V was obtained in 15.2% yield of theoretical .

$$\text{Found \%: C 68,07; 68,04; H 10,88; 10,95; Si 12,89; 12,99}$$
$$C_{12}H_{22}OSi. \text{ Calculated \%: C 68,57; H 10,47; Si 13,33.}$$

Action of triethylsilane on n-propylvinylethynylcarbinol. 31 g of the carbinol, 29 g of triethylsilane, and 2 ml of 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol were used. On distillation the following fractions were obtained: I, b. p. 58-60°/2, 6.8 g; II, b. p. 81-83°/2, 3.8 g; III, b. p. 83-84°/2, 2.1 g; IV, b. p. 88°/2, 4.7 g; V, b. p. 90-92°/2, 6.4 g; VI, b. p. 100-105°/2, 3.2 g. Fraction V was obtained in 10.7% yield of theoretical .

$$\text{Found \%: C 70,43; 70,13; H 10,40; 11,50; Si 11,52; 11,10}$$
$$C_{14}H_{26}OSi. \text{ Calculated \%: C 70,58; H 10,92; Si 11.76.}$$

Properties are given in Table 1.

Preparation of $CH_3 - CH - C \equiv C - CH - CH_3$ (with $OSi(C_2H_5)_3$ substituent) by counterpart synthesis. In a three-necked flask were placed 15 g of methylvinylethynylcarbinol and 12 g of pyridine, and 22 g of triethylchlorosilane was added dropwise; a white precipitate was obtained. After all the triethylchlorosilane was added, the flask was heated on a boiling water bath for 1.5 hours. After this the mixture was filtered and distilled in vacuo. The following fractions were obtained: I, b. p. 50-85°/6, 3.5 g; II, b. p. 84°/6, 7 g; III, b. p. 85°/6, 12 g. Fraction III had n_D^{20} 1.4553; d_4^{20} 0.8578; yield 36.5 of theoretical. Found MR_D 66.44; calculated 66.00.

$$C_{12}H_{22}OSi. \quad \begin{array}{llll} \text{Found } \% & C\ 67.86;\ 68.65; & H\ 10.80;\ 11.00; & Si\ 13.00;\ 13.00; \\ \text{Calculated } \% & C\ 68.57; & H\ 10.47; & Si\ 13.33. \end{array}$$

Hydroxyl was not detected.

Preparation of $n\text{-}C_3H_7 - CH - C \equiv C - CH = CH_2$ (with $OSi(C_2H_5)_3$ substituent). Under conditions similar to those described above, 10.5 g of the carbinol and 6.6 g of pyridine were used and 11 g of $(C_2H_5)_3SiCl$ was added. After distillation in vacuo the following fractions were obtained: I, b. p. 60-86°/3, 5.2 g; II, b. p. 86-87°/3, 5.8 g. Fraction II had n_D^{20} 1.4593; d_4^{20} 0.8589; yield 28.8% of theoretical. Found MR_D 75.79; calculated 75.26.

$$C_{14}H_{26}OSi. \quad \begin{array}{llll} \text{Found } \% & C\ 70.87;\ 70.98; & H\ 11.00;\ 11.30; & Si\ 11.60;\ 12.50 \\ \text{Calculated } \% & C\ 70.58; & H\ 10.92; & Si\ 11.76. \end{array}$$

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• See C. B. translation.

INVESTIGATION OF THE REACTION OF LEAD SELENIDE
WITH OXYGEN

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Lead selenide is used as a material for photoresistances sensitive in the infrared region of the spectrum. In order to improve the electrical characteristics, the photoresistant layers are heated in the air. In connection with this process it is necessary to determine the composition of the oxidation products and their effect on the electrical properties of PbSe. The problem presented is important also for the correct interpretation of the processes of roasting sulfide ores, one of the components of which is lead selenide.

In work by Willman [1] it was established electronographically that layers of PbSe (500-10,000 A) were oxidized completely at 350° after 10 minute heating in air. However, the oxidation products were not identified because of the absence of data in the literature. The kinetics of the oxidation of PbSe by oxygen were studied over the range 25-280° [2]. It was shown that at first the diffusion of oxygen ions takes place into vacant places in the selenium, and then selenium is replaced by oxygen. The process of reaction of PbSe with oxygen was studied by us manometrically, with x-ray and chemical analysis of the oxidation products.

EXPERIMENTAL

The starting PbSe was prepared by fusing stoichiometric quantities of the components in evacuated, sealed ampoules [3] Investigation of the rate of reaction of PbSe with oxygen with decreased gas pressure in the system was carried out in the apparatus shown schematically in Fig. 1. The volume of the working space and the temperature distribution along the furnace were determined in advance. The initial pressure of the oxygen was 200 mm Hg. A weighed sample (1.000 ± 0.0002 g) of vacuum-distilled and carefully ground PbSe in a platinum boat was placed in a quartz reactor. In all the experiments the major quantity of oxygen entering into the oxidation was calculated, and when possible (at temperatures of 610, 660°) the change in weight of the boat with the sample was determined. The kinetics of the oxidation were studied polythermally (20-800°) and isothermally at 610, 660, 750, and 800°. The investigation was qualitative in character, since the absolute magnitude of the surface of the samples was not determined. Figure 2 shows the differential polytherm obtained for the oxidation of PbSe with a correction for the thermal expansion of the oxygen in the volume of the reactor. The oxidation of PbSe under our conditions began at 300-350° and proceeded with appreciable speed at 560-600°. The maximum rate was observed at 640-680°. The crest in the curve (Fig. 2) apparently is connected with breakdown of the film of original oxidation product [4].

In an isothermic study of the oxidation of PbSe, the sample was heated in an atmosphere of argon, which was evacuated to achieve stable temperature conditions, and the system was filled with oxygen. In Fig. 3 the isotherms for the oxidation of PbSe are shown. The high reaction rate observed during the first moments of the reaction is connected with ignition of the PbSe. This is indicated by a rise in the temperature and fusion of the surface. Ignition is connected with the exothermic nature of the reaction and the low rate of heat emission under our conditions. At 610° the oxidation practically stops after energetic reaction in the first 5 minutes, and it proceeds thereafter according to a linear relationship. The temperature relationship of the isothermic oxidation is complex and does not have a well-defined interpretation.

TABLE 1

Results of Investigation of Oxidation Products of PbSe

Oxidation temp., °C	Change in wt of selenide (g)	Duration of expt. (min)	Amt. of O_2 entering oxidation (moles)	Pb found (%)	Se^{4+} found (%)	Phases detected[*]
610	+0.1189	310	0.00518	63.75	20.58	$PbSeO_3$
660	−0.1441	350	0.00559	72.85	9.97	Phase A
700	—	90	0.00551	70.60	12.18	Phase A + $PbSeO_3$
750	—	90	0.00546	70.56	12.51	Phase A + $PbSeO_3$
800	—	70	0.00546	77.09	7.35	Phase A
Polytherm	+0.0481	100	0.00448	69.63	14.51	Phase A + $PbSeO_3$

[*] Powdergrams obtained on Fe−K radiation.

Notes: 1. For complete oxidation of 1 g of PbSe according to the scheme $PbSe + {}^3/_2 O_2$, 0.00524 mole of O_2 is required. 2. The theoretical change in weight for 1 g of selenide in the conversion $PbSe \rightarrow PbSeO_3$ is + 0.1677 g and in the conversion $PbSe \rightarrow PbO$ is −0.2301 g.

TABLE 2

Results of Indexing X-ray Diagram of Product of Isothermal Oxidation of PbSe with Oxygen at 600° (Phase A)

I	$\frac{1}{d^2}$ expt.	hkl	$\frac{1}{d^2}$ calc.	I	$\frac{1}{d^2}$ expt.	hkl	$\frac{1}{d^2}$ calc.	I	$\frac{1}{d^2}$ expt.	hkl	$\frac{1}{d^2}$ calc.
1	0.0920			3	0.2608	200	0.2603	1	0.6621	222	0.6598
5	0.1000	101	0.0997	4	0.2693	112	0.2694	3	0.6864	114	0.6870
3	0.1305	110	0.1302	4	0.3607	211	0.3602	2	0.7255	302	0.7249
3	0.1388	002	0.1392	3	0.3773	103	0.3783	5	0.7784	312	0.7798
1	0.1545			3	0.3996	202	0.3995	1	0.8073		
1	0.1876			2	0.5259	220	0.5248	3	0.8175	204	0.8171
1	0.1951			2	0.5569	004	0.5568	4	0.8835	321	0.8808
1	0.2049	102	0.2043	3	0.6210	301	0.6205	3	0.9002	303	0.8989
1	0.2316			3	0.6380	213	0.6386	4	0.9317	105	0.9331
1	0.2463			2	0.6525	310	0.6508				

TABLE 3

Results of Indexing X-ray Diagram of Residue after Oxidation of PbSe in Air for 27 Hours at 800° (Phase B)

I	$\frac{1}{d^2}$ expt.	hkl	$\frac{1}{d^2}$ calc.	I	$\frac{1}{d^2}$ expt.	hkl	$\frac{1}{d^2}$ calc.	I	$\frac{1}{d^2}$ expt.	hkl	$\frac{1}{d^2}$ calc.
5	0.0947	101	0.0955	1	0.3305	210	0.3323	1	0.6452		
3	0.1025	011	0.1025	3	0.3387	103	0.3396	2	0.6687	222	0.6703
3	0.1220	002	0.1220	3	0.3481	013	0.3465	2	0.6763	031	0.6785
1	0.1290			1	0.3607			2	0.6875	311	0.6882
3	0.1371	110	0.1370	4	0.3634	211	0.3628	2	0.7146	130	0.7131
1	0.1482			4	0.3843	121	0.3836	3	0.7501	204	0.7483
1	0.1502			2	0.4125	113	0.4116	5	0.7859	132	0.7876
1	0.1858	102	0.1871	1	0.4750	122	0.4754	1	0.8310	015	0.8345
1	0.1948	012	0.1940	1	0.4904			4	0.8403	124	0.8391
1	0.2377			3	0.5536	104	0.5531	3	0.8720	320	0.8735
5	0.2600	112	0.2591	3	0.6143	301	0.6162	4	0.9099	230	0.9083
1	0.2668			2	0.6234	114	0.6251	3	0.9314	313	0.9322
2	0.2884	020	0.2880	4	0.6289	123	0.6276	4	0.9401	231	0.9388

<u>Investigation of oxidation products.</u> The samples of PbSe oxidized at different temperatures were chemi-
cally analyzed for lead and Se^{4+} [4].

From the number of moles of oxygen entering into the oxidation of 1 g of PbSe (1.5 moles of O_2 to 1 mole
of PbSe), it can be assumed that the oxidation proceeds mainly according to the equation PbSe + $^3/_2$ O_2 = PbSeO$_3$.
In fact, it has been shown from x-ray data that the main oxidation product at 610° is lead selenite. This result
is in agreement with data from chemical analysis and with the increase in weight of the sample.

In the products of oxidation of PbSe at higher temperatures, the presence of a new phase has been estab-
lished, the x-ray pattern of which (with the exception of very weak lines) could be indexed by the parameters of
a tetragonal volume-centered cell a = 3.92 ± 0.01 kX, c = 5.37 ± 0.01 kX (cf. Table 2).

The product of oxidation of PbSe in air for 27 hours at 800° was a new phase. Its Debye crystallogram was
indexed with the parameters of a rhombic volume-centered cell a = 3.92 ± 0.01 kX, b = 3.73 ± 0.01 kX, c =
= 5.72 ± 0.01 kX (cf. Table 3).

Besides the lines of the tetragonal phase, in some x-ray patterns of the oxidation products lines for lead
selenite were present. Since thermal breakdown of lead selenite occurs with the formation of the same phases, it
is likely that when PbSe is oxidized the selenite is first formed and then decomposes. As has already been indi-
cated, weak, unindexed lines are observed in the x-ray patterns for the tetragonal and rhombic phases. Their
intensity and position is not dependent on the conditions under which the preparations are obtained, therefore,
they can scarcely be explained by the presence of contaminants. Probably the cell parameters given above for
these phases correspond to subcells and the weak lines are those of the superstructures.
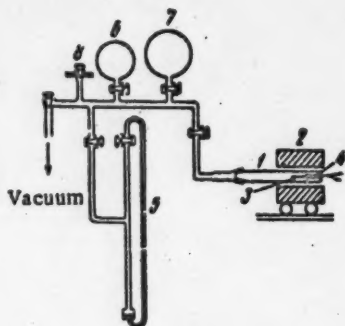
Fig. 1
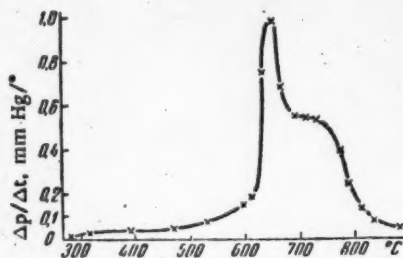
Fig. 2

The chemical analysis of the samples and the x-ray patterns,
which correspond to the pure tetragonal phase obtained by different
methods (isothermal oxidation of PbSe at 660 and 800°, thermal de-
composition of PbSeO$_3$ at 1100°) show that the composition of this
phase is variable, although no change was detected in the param-
eters of the lattice.

The results of the chemical analytical studies indicate that
Pb^{4+} or Se^{6+} should be present in the products of the oxidation of
PbSe and of the thermal decomposition of lead selenite and sele-
nate. This assumption is confirmed by the fact that the amount of
oxygen entering into the oxidation in all the experiments was some-
what larger than that calculated from the ratio of 1.5 moles of O_2
to 1 mole of PbSe (cf. Table 1).

The tetragonal and rhombic phases, apparently, are struc-
turally similar to some of the oxides of lead, as can be seen from
the comparison (cf. Table 4) of the cell parameters and volumes
calculated for one formula unit of PbO$_n$ or (Pb, Se)O$_x$ (all cells
are volume centered). The data for PbO$_{1.6}$ were recalculated from
the original data for the oxide Pb$_5O_8$. In the opinion of the authors
of [6], one formula unit of Pb$_5O_8$ corresponds to a cell with the
parameters a = 5.508 kX and c = 5.460 kX, which, however, leads
to some discrepancy in the calculated and experimental density
values ρ_{x-ray} = 11.6, ρ_{expt} = 9.51). In our opinion it is more cor-
rect to regard this phase as the nonstoichiometric PbO$_{1.6}$ (from the
authors' data it can be concluded that there is some variation in
the composition of this phase). Calculation of the density on the
assumption that 4PbO$_{1.6}$ correspond to a cell leads to the value
ρ_{x-ray} = 9.32, which is close to the ρ_{expt}. The observed syste-
matic absence of lines that do not satisfy the condition of a face-centered cell also agrees with our interpretation.

Probably both of the phases obtained by us can be regarded as phases of variable composition (Pb, Se)$_x$. In
the system PbO—O$_2$, phases with a greater oxygen content than PbO are unstable at high temperatures, a fact that

TABLE 4

Parameters of Lattice and Volume of
Some Phases of PbO_n and $(Pb_1Se)O_4$

Composition	a, Å	b, Å	c, Å	V, Å³
PbO (*)	$3.947\pm$ ± 0.006	—	$4.988\pm$ ± 0.008	39
$PbO_{1.6}$	3.805	—	5.460	41.5
$(Pb, Se)O_x$ (rhombic)	3.03	3.74	5.74	42.1
$(Pb, Se)O_x$ (tetrag.)	3.03	—	5.38	41.4
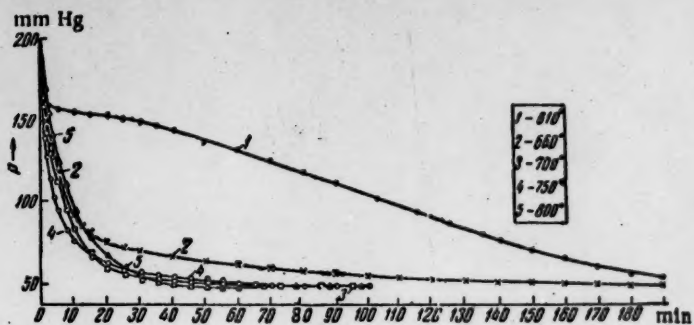
Fig. 3

apparently is connected with the presence in them of Pb^{4+}. The presence of tetravalent selenium stabilizes the phases with a greater oxygen content. The similarity of the radii of Se^{4+} (0.76 Å) makes isomorphic replacement possible. The presence of weak superstructural lines is connected with some ordering of the position of the Pb and Se atoms.

The structures of CaF_2, Mn_2O_3, and PbO are very similar with regard to the arrangement of the cation, although their composition varies from AX_2 to AX. The arrangement of the cations in $(Pb, Se)O_x$ is most similar to PbO and $PbO_{1.6}$. For the structural types mentioned, cases are known of deviation from the stoichiometric composition. Such facts are especially numerous for structures of the type of $CaF2$ with both the formation of anion vacancies and excess anions in voids of the lattice. Probably $PbO_{1.6}$ is related to one of these phases. The composition and structure of the phases of $(Pb, Se)O_x$ may possibly be intermediate between PbO and a structure of the type of Mn_2O_3.

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THE EFFECT OF PRESSURE ON THE SPECIFIC HYDROGENATING
ACTIVITY OF PLATINUM ON ALUMINA GEL

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The preparation of curves showing the relationship of the specific catalytic activity of metals to the amount of them on the carrier is a convenient method of studying the structure of the active layers of adsorption catalysts. [1]. Much information of this kind has been obtained for platinum on carriers in hydrogenation in the liquid phase at atmospheric pressure [1, 2]. It is known that a change in the pressure of the hydrogen in the gaseous phase changes the charging of the catalyst surface with hydrogen, and often also changes the order of the catalytic reaction, i. e., its limiting stage. It was of interest to us to investigate how the hydrogen pressure affects the relationship of the specific hydrogenating activity of platinum to the amount of platinum on the carrier.

As an example, we studied the hydrogenation of dimethylvinylethynylcarbinol [$(CH_3)_2C(OH)C-C\equiv C-$ $-CH-CH_2$, hereafter referred to as DVEC] and of picric acid under atmospheric and increased hydrogen pressure the activity of platinum supported in small amounts on alumina gel. Sixteen catalysts were prepared with platinum contents from 0.081 to 1.78%. These surface loads are in the range of thousandths of a monolayer.

The alumina gel was prepared by precipitation of aluminum hydroxide with ammonia from a dilute solution of potassium aluminum alum. The gel was carefully washed free of SO_4^{2-} ions, dried, heated at 550° for four hours, and finely ground in an agate mortar. The platinum was deposited at room temperature from dilute aqueous solutions of $PtCl_4$ of different concentrations, with continuous shaking for two hours. In this time the platinum was quantitatively adsorbed on the alumina gel and was no longer detected in the filtrate or in the wash water. After being washed free of chloride ions, the catalysts were dried and then reduced in a current of purified electrolytic hydrogen while being heated to 360°. The catalysts, which had been cooled in an atmosphere of hydrogen, were transferred to flasks with ground stoppers, which were then stored in a desiccator with calcium chloride.

The DVEC was distilled in vacuo every 3-4 days and had an index of refraction n_D^{15} 1.4778 (agreeing with the literature). The picric acid was recrystallized from 50% alcohol. For the hydrogenation experiments, an apparatus was used that permitted maintaining a constant hydrogen pressure of one to three atmospheres during the reaction [3]. The temperature of the experiments was 35°. The hydrogen pressure was atmospheric, or 1 or 2 atmospheres in excess. The medium was 50% alcohol. Before the hydrogenation, the catalyst was shaken in an atmosphere of hydrogen for 30-40 min, then the DVEC was added (0.491 g, 300 ml of H_2 at N. T. P.). At the end of the hydrogenation of the carbinol, picric acid (0.909 g, 78 ml of H_2 at N. T. P.) in alcoholic solution was introduced into the reaction mixture. Each experiment was repeated twice on fresh 0.4-g samples of catalyst. The reproducibility of the experiments averaged about 10%. When DVEC was hydrogenated at all pressures, the rate slowly increased, reaching a maximum after the absorption of $^2/_3$ of the theoretically required hydrogen, and then quickly decreased. The kinetic curves for picric acid have an S-shape.

The activity of the catalysts was determined by several methods: for DVEC it was determined by the inverse values of the time for half-hydrogenation and of the time for absorption of $^2/_3$ of the theoretically necessary amount of hydrogen (in minutes), by the maximum rate and by the average rate of absorption of hydrogen on the portion of the curve up to the maximum; for picric acid it was determined by the inverse values of the time for half-hydrogenation and of the time for absorption of 45 ml of hydrogen (region of sharp decrease in rate), and also
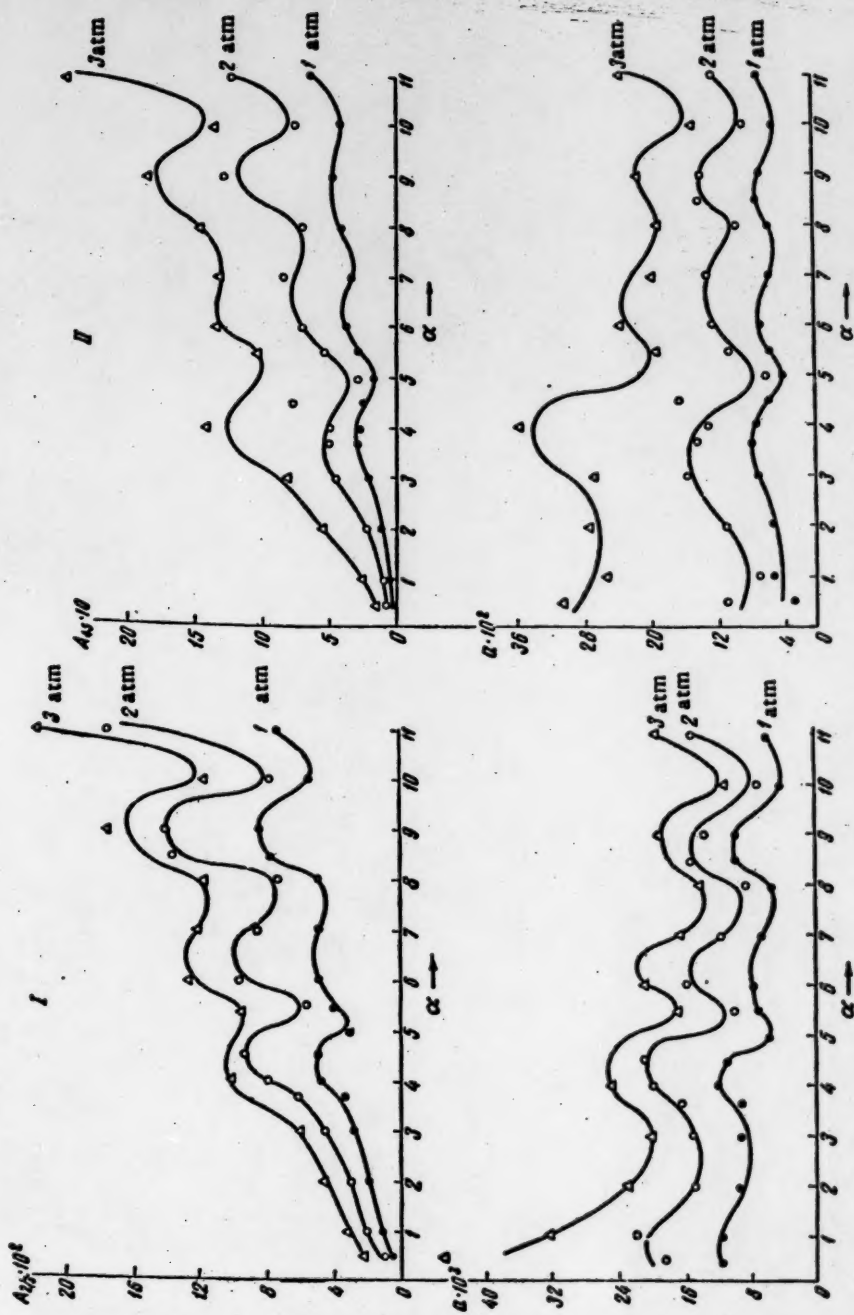
Fig. 1. Total (A) and specific (a) activity of platinum supported on alumina gel in relation to the degree of loading (of the alumina gel surface with platinum) in the hydrogenation of dimethylvinylethynylcarbinol (I) and picric acid (II) at hydrogen pressures of 1, 2, and 3 atm.

by the average rate of absorption of hydrogen in this portion of the curve. All of the alternative methods gave similar results. The average values from two parallel experiments were used to construct the graphs. The specific activity was found by division of the total activity by the degree of loading, for which the unit of comparison was taken as 0.162 wt % of platinum.

The curves for the relationship of the total and the specific activity to the degree of loading are shown in Fig. 1. As can be seen, when the loading of the surface of the alumina gel with platinum increases, the activity of the catalysts rises, increasing approximately in proportion to the pressure. The maxima and minima in the curves are rather well repeated at all three pressures, so that it may be considered that they are not accidental. The specific activity of the platinum changes comparatively little over the whole course of the curves. Obviously all of the platinum deposited participates in the reaction, but various combinations of the atoms obtained at different concentrations have more or less activity.

The general aspect of the relationship of the specific activity to the degree of loading is preserved at all of the pressures studied. This indicates that the character of the participation of the active layers of platinum in the hydrogenation reaction does not change with an increase in hydrogen pressure. It is interesting that this character is the same for the hydrogenation of the unsaturated bonds of DVEC and of the nitro groups of picric acid. Similar relationships of the specific activity to the degree of loading for the hydrogenation of the triple bond of dimethylvinylethynylcarbinol and of the nitro groups in picric acid have been obtained by us previously on platinized carbon [2], although other authors [4] have found that carbon–carbon bonds are hydrogenated at a doublet, and the nitro group at a single platinum atom.

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POLAROGRAPHIC REDUCTION OF DERIVATIVES
OF 2-NITROFURAN AND 2-NITROSELENOFURAN

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In previous communications, two of us have shown the applicability of the polarographic method to the analytical determination of nitrofurans in aqueous solutions, including the fluids from an organism [1], and the possibility of using this method to determine the solubility in water of substances of this class [2]. We also reported on the mechanism of polarographic reduction of 2-nitrofuran [3] and some of its derivatives that are used as chemotherapeutic agents [4].

In the present work we show the effect of substituents in the 5-position of the furan and selenofuran rings on the polarographic reduction of the nitro group in the 2-position. A number of authors have already shown the suitability of Hammet's equation for the integration of data from the polarographic investigation of similar compounds of both the aromatic [5-8] and the heterocyclic [9-11] series. The present investigation supplements the material in the literature with new examples and permits comparison of derivatives of 2-nitrofuran and 2-nitroselenofuran with nitro derivatives of the aromatic series.

EXPERIMENTAL

The 25 derivatives of 2-nitrofuran and 2-nitroselenofuran (I-XXV) studied in this work are given in Table 1.

In order to obtain comparable data for the series of compounds under investigation, all of the compounds were studied under strictly identical conditions: in aqueous solutions with a 10^{-4} M concentration of the nitro compound, at constant pH values in Britton-Robinson universal buffer solutions in the pH range from 2 to 11, on a background of 0.1 N KCl in a thermostatic apparatus at 20°. The potentials were read with respect to a saturated Hg_2Cl_2 electrode. The curves were obtained on a photorecording Heyrovsky polarograph, and the pH of the solution was determined electrometrically. From the data obtained, the half-wave potentials ($E_{1/2}$ were calculated in relation to the pH, and the values of the diffusion currents (i_d) also were found at various pH and the number of electrons taking part in the electrode reaction was calculated by the Il'kovich equation.

In the polarograms for the nitro compounds studied, there is one or several waves, depending on the nature of the compound and the pH range. The first wave, lying at the most negative potential, is dependent on the four-electron reduction of the nitro group to hydroxylamine, and the subsequent waves on the further reduction of the intermediate hydroxylamine derivative to amine or the reduction of other functional groups in the molecule (C= O, C= N-). The complete data on the relationship of $E_{1/2}$ and i_d to pH for all the waves will be presented elsewhere [12, 13]; here only the relations for the first four-electron wave of the reduction of the nitro group, necessary for the discussion, are given (Table 1). $E_{1/2}$ for this wave depends on the pH and the concentration of the nitro compound in the solution (becoming more negative with an increase in these parameters), and the values of i_d in acid and neutral media remain constant at various pH. The electron reaction is irreversible, and the waves have the character of diffusion waves.

TABLE 1

Relations of Polarographic Waves for the Reduction of the Nitro Group (10^{-4} M Aqueous Solution of Nitro Compound)

No.	Formula	$E_{1/2}$, v
I	R—H	−0,04—0,053 pH
II	R—Br	+0,04—0,056 pH
III	R—CHO	{+0,08—0,041 pH −0,01—0,042 pH
IV	R—COCH₃	+0,03—0,036 pH
V	R—CH<COOCH₃ COOCH₃	+0,02—0,042 pH
VI	R—COCH₂OH	+0,03—0,036 pH
VII	R—COOH	+0,05—0,056 pH
VIII	R—COOC₂H₅	+0,02—0,037 pH
IX	R—CH=CH—CHO	+0,07—0,038 pH
X	R—CH=CH—COCH₃	+0,02—0,035 pH
XI	R—CH=CHNO₂	+0,04—0,034 pH
XII	R'—H	−0,06—0,048 pH
XIII	O₂N—⟨ ⟩—NO₂ (Se)	{+0,12—0,057 pH 0—0,065 pH
XIV	R'—CHO	+0,03—0,036 pH
XV	R'—COCH₃	+0,01—0,035 pH
XVI	R'—COOH	+0,045—0,051 pH
XVII	R'—CH=CH—CHO	+0,06—0,040 pH
XVIII	R'—CH=CH—COOH	+0,07—0,054 pH
XIX	R—CH=N—NH—CONH₂	+0,06—0,050 pH
XX	R—CH=CH—CH=N—NHCONH₂	+0,085—0,054 pH
XXI	R—CH=N—N—CH₃ OC CO NH	+0,06—0,048 pH
XXII	R—CH=CH—CH=N—N—CH₃ OC CO NH	+0,08—0,047 pH
XXIII	R—CH=N—N—CO O H₂C—CH₂	+0,06—0,047 pH
XXIV	R'—CH=N—NHCONH₂	+0,04—0,039 pH
XXV	R'—CH=N—N—CH₃ OC CO NH	+0,04—0,046 pH

$R = O_2N-⟨\ ⟩_O-$; $R' = O_2N-⟨\ ⟩_{Se}-$

DISCUSSION OF RESULTS

The polarographic reduction of derivatives of 2-nitrofuran and 2-nitroselenofuran follows the same mechanism as the reduction of derivatives of nitrobenzene [7] and 2-nitrothiophene [11]. The half-wave potentials of the nitro derivatives of all of the series mentioned also lie close to each other and as a result of the presence of conjugated double bonds in the molecule they are considerably more positive than those of the aliphatic and alicyclic nitro compounds. Comparison of the series mentioned leads to the conclusion that the nitro group in derivatives of 2-nitrofuran is the most easily reduced; reduction in the derivatives of 2-nitrothiophene and 2-nitroselenofuran is more difficult by 20-30 mv, and in derivatives of nitrobenzene is more difficult by 40 mv than in 2-nitrofuran. The increase in the potentials in the series of heterocyclic isologs is connected with a decrease in the electron displacement from the unshared electron pair in the order O > S > Se. In particular, the derivatives of 2-nitroselenofuran are more similar in their polarographic behavior to the derivatives of nitrobenzene than to those of 2-nitrofuran, which also is in agreement with observations of some of the chemical properties of this series of compounds [14].

Demonstrations of the effect of minute differences in the nature of the heteroatom on $E_{1/2}$ for the polaro-graphic reduction of the nitro group (or of any other functional group on the ring) is hardly feasible in view of the closeness of the potentials, since the differences lie within the limits of error of the experiment. More re-fined investigations maintaining absolutely identical experimental conditions, however, might solve this problem and also give, along with the values for the dipole moments, a new criterion for the characterization of hetero-cycles.

Study of a series of derivatives permits quantitative evaluation of the effect of substituents on the polaro-graphic reduction of the nitro group with respect to the change in $E_{1/2}$ for the substituted compound in compari-son to the unsubstituted. In the nitrobenzene and nitrofuran series this change can be expressed by the Hammet equation:

$$E_{1/2}^{(x)} - E_{1/2}^{(0)} = \rho\sigma,$$

where ρ is a constant for the given reaction, constant for a whole series of derivatives; σ is a constant charac-teristic of the substituent X in different reactions.

From our data it follows that this is accurate for derivatives of 2-nitrofuran and 2-nitroselenofuran, if the same values of σ are taken for the substituents on the heterocycle as for the aromatic series, and the calculated values of $\Delta E_{1/2}$ and ρ are compared at the same pH in weakly acid medium.

Substituents with a negative mesomeric effect facilitate reduction, and $\Delta E_{1/2}$ in the series of 5-substituted heterocyclic 2-nitro compounds has approximately the same values as for p-substituted derivatives of nitrobenzene; consequently, the behavior of 2,5-substituted derivatives of five-membered heterocycles corresponds to the be-havior of p-substituted derivatives of the aromatic series at the same time that it differs from that of m-substi-tuents, which in general agrees with the rules of orientation developed in a study of the reactivity of substituted furans. More exact polarographic measurements are required as well as calculation of exact values of σ from the dissociation constants of the 5-substituted furancarboxylic acids to reveal exact differences between the values of ρ in aromatic and heterocyclic series and quantitatively evaluate the effect of the heteroatom on the polarographic behavior and the reactivity of the five-membered heterocycles.

The effect of a substituent through a supplementary $-CH=CH-$ group in a side chain in some cases (for 5-nitrofurfurylidenehydrazones) somewhat facilitates the reduction of the nitro group, but in other cases it does not change the reduction picture; in general this effect is small.

The reduction of 5-nitrofurfural follows an unusual pattern. The four-electron wave for the reduction of the nitro group in this case is split, and of the two waves one has in part a kinetic character. It may be assumed that in aqueous solutions of 5-nitrofurfural the following equilibrium occurs:

(a)   (b)
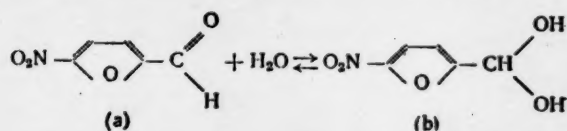
where the more positive wave corresponds to reduction of (a) and the more negative to reduction of (b). Similar conclusions were drawn from the results of the determination of the dipole moments [15] and the study of the ab-sorption of 2-nitrofurfural in the ultraviolet [16]. In contrast to its isolog, 5-nitroselenofurfural is reduced nor-mally (like p-nitrobenzaldehyde), from which it follows that this compound is not hydrated in aqueous media.

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NEW AMINO DERIVATIVES OF 2-PHENYLINDANDIONE-1,3

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In a study of amino derivatives of 2-substituted indandiones-1,3 [1-4] it was found that many of them have pronounced physiological action [5, 6] which depends to a great degree on the amino group introduced in the case of any one indandione. A dialkylaminoalkyl group attached to nitrogen or oxygen is characteristic of many physiologically active substances, especially anesthetics, spasmolytics, antimalarials, and other compounds [7, 8]. By introducing a dialkylaminoethyl group into the 2-amino-2-phenylindandione-1,3 molecule, we would obtain a N,N-dialkyl-N'-phenylindandionyl-(2)-ethylenediamine (II). Thus, N-substituted ethylenediamines are in- cluded among compounds having strong plasmolytic and antihistaminic action [9]; it was our purpose to synthe- size the corresponding derivatives of indandiones—2-phenylindandione-1,3 first. Several routes for carrying out this synthesis are conceivable.

IIa R = R' = C_2H_5

IIb R and R' = $-(CH_2)-$
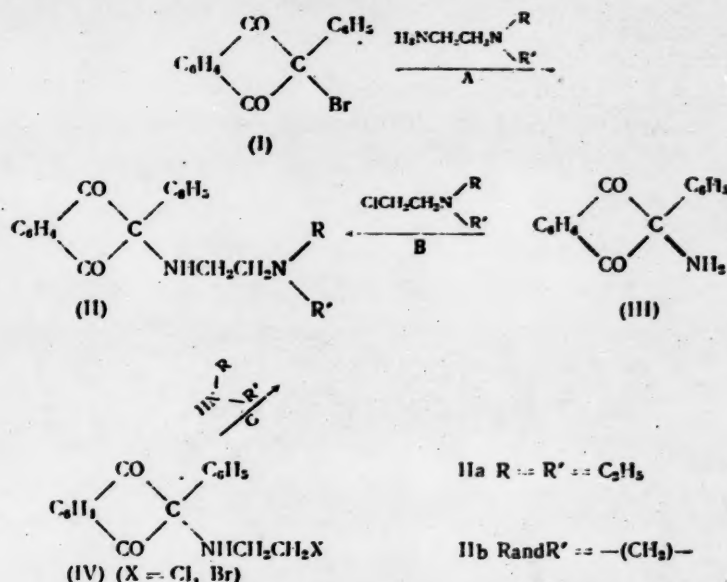
We rejected variant A because the corresponding ethylenediamine was not available and because, to judge from experience, 2-bromo-2-phenylindandione-1,3 (I) reacts both with primary and tertiary amino groups, which would lead to a mixture of substances. In order to test variant B we melted 2-amino-2-phenylindandione-1,3 (III) [11] with β-dimethylaminoethyl chloride hydrochloride at 120-150°. It was found that the expected conden- sation did not occur, but self-condensation of the 2-amino-2-phenylindandione-1,3 apparently took place with formation of compound V. The nitrogen content corresponds to the proposed formula; a separate work will be de- voted to a detailed study of this interesting reaction and to determination of the structure of the substance obtained.

(V)
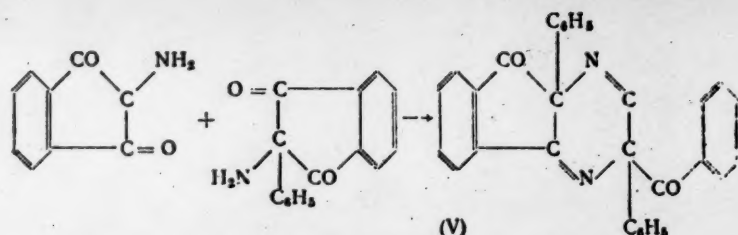
The synthesis of (II) was accomplished by variant C, by treating a 2-β-haloethylamino-2-phenylindandione-1,3 (IV) with diethylamine or piperidine; a method of preparing (IV) from either 2-β-hydroxyethylamino-2-phenylindandione-1,3 or 2-ethyleneimino-2-phenylindandione-1,3 was recently developed by us [10]. 2-β-Chloroethylamino-2-phenylindandione-1,3 reacts with diethylamine with difficulty even on boiling in dioxane solution. The reaction with piperidine goes somewhat more readily. On the contrary, 2-β-bromoethylamino-2-phenylindandione-1,3 reacts both with diethylamine and piperidine even at room temperature to form the expected compounds IIa and IIb. They were isolated in the form of the dihydrochlorides, which were solid, white, very hygroscopic salts that could not be recrystallized, but gave satisfactory results in analysis even without crystallization when pure starting materials were used. The salts are soluble in water; the aqueous solutions are faintly greenish-yellow and give an acid reaction. Evidently, the dihydrochlorides (VI) in aqueous solution are partly hydrolyzed to the monohydrochlorides (VII). As our previous investigations showed, 2-amino-2-phenylindandiones are but weak bases, and their salts are easily hydrolyzed in aqueous solution, giving the colored bases
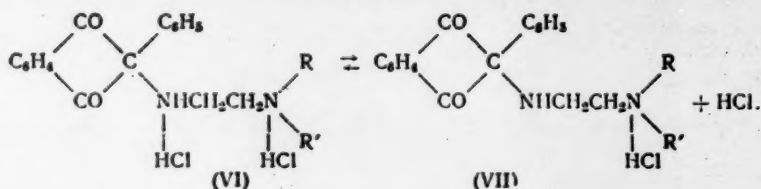
The free bases (IIa and IIb) are viscous, greenish-yellow oils and have not yet been isolated in pure form.

On interaction of 2-β-bromoethylamino-2-phenylindandione-1,3 with tertiary bases—triethylamine, pyridine, and isoquinoline—the corresponding tetrasubstituted ammonium salts (VIII) are obtained. These are greenish-yellow, crystalline substances, very soluble in water and alcohol and insoluble in ether.
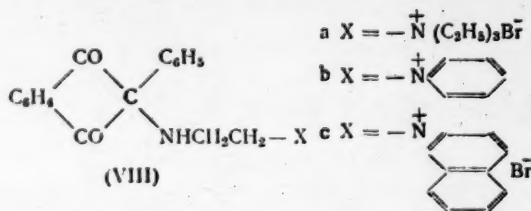
The physiological activity of the new amino derivatives of 2-phenylindandione-1,3 that have been prepared is being studied.

EXPERIMENTAL

2-(β-Piperidinoethylamino)-2-phenylindandione-1,3 dihydrochloride (IIb). a) To a suspension of 3 g of 2-β-chloroethylamino-2-phenylindandione-1,3 (IV) hydrochloride in 25 ml of dry dioxane, 2.7 ml of piperdine in 10 ml of dioxane was added; the mixture boiled 3.5 hours in an oil bath (bath temperature about 140°). On cooling, absolute ether was added; after some time the separated piperidine hydrochloride (2 g) was filtered out and the filtrate evaporated in vacuo. The oily residue was again dissolved in abs. ether and the solution boiled with activated charcoal, dried with anhydrous sodium sulfate, and saturated with dry hydrogen chloride. Yield

3.5 g (93%) of the white dihydrochloride. The salt was immediately placed in a heated vacuum desiccator. The salt was very hygroscopic and quickly deliquesced in air. M. p. 150-154° (dec.). It dissolved in water, forming a faintly yellowish solution which foamed on shaking; the solution gave an acid reaction. b) To a solution of 4 g of 2-(β-bromoethylamino)-2-phenylindandione-1,3 in 20 ml of abs. ether was added 2.5 ml of piperidine in 10 ml of abs. ether. The reaction began immediately, and piperidine hydrobromide precipitated. On the next day the precipitate was filtered out and the filtrate worked up as in (a). Yield, 4.4 g (90%) of the dihydrochloride. M. p. about 150° (dec.).

$$\text{Found} \quad \%: \text{N } 6.46 \text{ (a); } 6.48 \text{ (6)}$$
$$C_{22}H_{24}O_2N_2 \cdot 2HCl. \text{ Calculated} \quad \%: \text{N } 6.65$$

2-(β-Diethylaminoethylamino)-2-phenylindandione-1,3 dihydrochloride (IIa). To a solution of 4 g of 2-(β-bromoethylamino)-2-phenylindandione-1,3 in 20 ml of ether and 5 ml of dioxane was added 3 ml of diethylamine in ether. The solution was left for 2 days at room temperature and then heated for one-half hour in a water bath. It was then further treated as in the preparation of the piperidine derivative. Yield 4.6 g (96.5%) of the white salt. Very soluble in alcohol and chloroform, slightly soluble in acetone, and insoluble in ether. M. p. 110-112° (dec.). Aqueous solutions gave an acid reaction and foamed on shaking.

$$\text{Found } \%: \text{N } 6.36; \text{ } 6.48$$
$$C_{21}H_{25}O_2N_2 \cdot 2HCl. \text{ Calculated } \% \text{ N } 6.83$$

Picrate. From an aqueous solution of the salt by adding picric acid. M. p. 151-153° (from alcohol). On analysis, corresponded to the monopicrate.

$$\text{Found } \% \text{ N } 12.53$$
$$C_{27}H_{27}O_9N_5. \text{ Calculated } \% \text{ N } 12.38$$

N-(2-Phenylindandion-1,3-yl(2))-β-aminoethyltriethylammonium bromide (VIIIa). To 2 g of 2-(β-bromoethylamino)-2-phenylindandione-1,3 in 10 ml of abs. dioxane was added 1 ml of triethylamine in 5 ml of abs. dioxane, and the mixture was heated for 3 hours in an oil bath (105-110°). At the bottom of the flask an oily liquid collected, which solidified on cooling. The dioxane was distilled off in vacuo, the residue was dissolved in abs. alcohol, the solution was boiled with activated charcoal and filtered, and the filtrate was diluted with abs. ether. Yield 1.8 g (72.7%) of the greenish-yellow salt. M. p. 188°. Very soluble in water and alcohol. Aqueous solutions were greenish-yellow; on addition of hydrochloric acid they were decolorized.

$$\text{Found } \% \text{ N } 6.86$$
$$C_{23}H_{29}O_2N_2Br. \text{ Calculated } \% \text{ N } 6.59$$

N-(2-Phenylindandion-1,3-yl(2))-β-aminoethylpyridinium bromide (VIIIb). To a solution of 2 g of 2-(β-bromoethylamino)-2-phenylindandione-1,3 in abs. ether was added 1 ml of pyridine in 10 ml of abs. ether and the mixture boiled for 1 hour. A greenish-yellow precipitate formed. The mixture was left tightly sealed. for 2 days, boiled for 1 more hour, and again left for 2 days. The ether was distilled off in vacuo, the greenish residue dissolved in abs. alcohol, the solution boiled with activated charcoal and filtered, and the filtrate diluted with ether. Yield 0.9 g (36.6%) of greenish-yellow crystals. M. p. 215°. Very soluble in water and alcohol, the solutions being greenish-yellow.

$$\text{Found } \% \text{ N } 6.68$$
$$C_{22}H_{19}O_2N_2Br. \text{ Calculated } \% \text{ N } 6.62$$

N-(2-Phenylindandion-1,3-yl(2))-aminoethylisoquinolinium bromide (VIIIc). This was prepared as in the preceding. From 2 g of 2-(β-bromoethylamino)-2-phenylindandione-1,3 and 1 ml of isoquinoline there was obtained 1 g (36.3%) of a greenish-yellow substance with m. p. 197° (from alcohol, ether being added). Aqueous solutions were greenish-yellow.

$$\text{Found } \% \text{ } 5.85$$
$$C_{26}H_{21}O_2N_2Br. \text{ Calculated } \% \text{ N } 5.92$$

2,3(CO); 5,6(CO)-dibenzoylene-3,6-diphenyl-3,6-dihydropyrazine (V?). Two g of (III) and 2 g of β-dimethylaminoethyl chloride hydrochloride were melted together during 15 minutes at 120-150°, the melt boiled in dioxane, and the residue crystallized from alcohol, ether being added. A 1.5 g quantity of the original HCl salt was recovered. The dioxane filtrate was evaporated in vacuo and the residue gradually diluted with water. At first a dark resin separated, which was removed. On further dilution with water a brownish-yellow precipitate formed, which was recrystallized from dioxane after treatment with activated charcoal and dilution with water. Yield 0.3 g (16.2%) of yellow crystals. M. p. 262-265° (dec.).

Found %N 5.99
$C_{30}H_{18}O_2N_2$. Calculated % N 6.39

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PHOTONEUTRON METHOD OF DETERMINING
THE DEUTERIUM CONCENTRATION IN NATURAL WATER

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(Presented by Academician A. P. Vinogradov, July 17, 1959)

In the ordinary method of determining the deuterium concentration in water, measurement of its physical constants—density or refractive index—is usually envisaged. Measurement of constants is pointless when the water contains impurities. Furthermore, if it is taken into account that water contains not only H and D, but also O^{16}, O^{17}, and O^{18} and their isotopic composition is not constant, the preparative operations include both thorough removal of impurities from the water and normalization of the isotopic composition of oxygen in the sample being investigated [1]. These inconveniences, as well as a possible source of error connected with alteration of the isotopic composition of hydrogen in the process of preparing the sample, are avoided in the method of direct determination of the deuterium concentration by using the reaction of photocleavage of the deuteron [2, 3].

Calculations show that if a source of γ-radiation of suitable intensity is used in combination with an efficient method of retarding and recording neutrons, the deuterium concentration in water can be determined quite easily and quickly with an accuracy of $\pm$ 1% by this procedure.

The method consists essentially in the following: the water sample being analyzed is irradiated with a stream of γ-quanta. The neutron flux generated in the reaction $D^2 (\gamma, n) H^1$ is recorded by a suitable counter. The threshhold of this reaction is equal to 2.22 Mev and its cross section, to $1.2 \cdot 10^{-27}$ cm^2 [4].

Under standard conditions of measurement the number of neutrons emitted is proportional to the deuterium concentration in the water. On determining the counting rate for a standard water sample and the one being investigated, the deuterium concentration in the latter is easily calculated.

The method of determining deuterium in water described above was experimentally tested, a Na^{24} γ-radiation source, whose γ-radiation had an energy of 2.76 Mev, being used. At this energy level only one element, Be, can emit neutrons on treatment with hard γ-quanta. The cross sections of the reaction (γ, n) for D_2O and Be are about the same.

The apparatus in which the determinations were carried out (Fig. 1) consists of a cylindrical lead block 1 placed inside a paraffin reflector 2. At the center of this block there is a void 3 of approximately spherical shape, with a volume of 600 cm^3, having three outlet tubes 4. 5, 6. In an annular gap in the lead are placed 20 proportional counters 7 filled with B^{10}-enriched boron trifluoride. The γ-radiation source is located in a cylindrical capsule 8 mm in diameter, placed at the center of the void.

The sample is introduced into the measuring chamber through 5 and drained out after measurement through outlet 6. Tube 4 prevents the formation of an air cushion in the measuring space.

In carrying out the measurements the initial power of the source was 126 $\pm$ 10% mC; in this case the counting rate from a 600-ml sample of natural water was 500 imp/minute, or 4 imp/minute per mC of Na^{24} with a background of 16 imp/minute, the background of the apparatus in the absence of the γ-source being 0.6 imp per minute per counter or 12 imp/minute. This small increase of background, observed on putting the source into the apparatus (4 imp/minute), is due to the presence of the thick lead shielding and the paraffin shell of the apparatus and proportional counters, which give milder operating conditions for the latter.
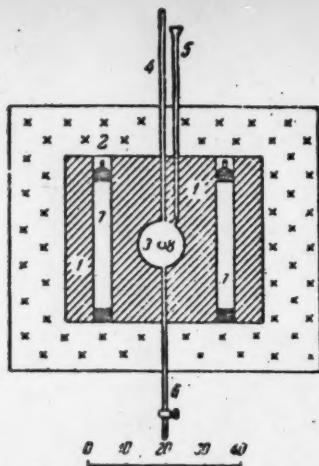
Fig. 1. Schematic vertical section of the apparatus for determining the deuterium concentration in water.

The use of such large quantities of sample for analysis created the need for efficient retardation of photoneutrons in order to increase the counting rate of the apparatus. The lead itself practically does not slow or absorb the neutrons, but it is an excellent medium for their diffusion [5].

Therefore, despite the fact that the possibilities of efficient retardation of neutrons in such constructions are limited, the efficiency of the apparatus proved to be considerable, about 2.5%.

An elementary calculation shows that half the photoneutrons are generated from a sample volume less than 100 ml, adjacent to the source. Hence, when small quantities of sample are used for analysis it would be very advantageous to use protium water for retardation. The preparation of the required amount of such water with a deuterium concentration of 10^{-5}% is now quite feasible [1].

The inconvenience of isotopic analysis of hydrogen, using Na^{24} consists in the fact that access to a "kettle" neutron source must be continually maintained; this is due to the shortness of the half-life of Na^{24}.

Results obtained. The short life of Na^{24} and the relatively small initial quantity of the latter on the one hand, and the fact that a considerable quantity of preliminary measurements had to be made, on the other, did not permit the authors to carry out the measurements with the required statistical accuracy or to limit the error of a single determination to ± 1.5-2.5%. Fourteen measurements of samples of artificial and natural water were made.

A linear relation between the counting rate and the deuterium content in water up to a D_2O concentration of 0.1784% was obtained (Fig. 2, I). The magnitude of the error due to impurities in the water was determined. The presence of elements with high effective neutron capture cross-section in the water, such as B, Cd, and Cl, may make the result of determination erroneous. The magnitude of this error was determined by measuring 4 water samples with the Cl^- concentrations: 0, 0.92, 0.91, and 2.9%. Experimental results are shown in Fig. 2, II. It was found that 0.24% Cl^- in the water decreases the result of determination of the D_2O concentration by 1%. Hence, the equivalent concentrations for boron and cadmium were found by calculation to be $3 \cdot 10^{-3}$ and $1.1 \cdot 10^{-2}$%, respectively.

The deuterium concentration in the water of the Moscow Aqueduct was determined by four independent measurements, without preliminary distillation; it proved to be equal to 0.0144 ± 0.0003 volume percent. The same concentration was found in the distillate of this water.

Possibilities of using long-lived irradiators in the apparatus. Not only Na^{24} may be used for these purposes, but also Y^{88} (T = 105 days), which also has a γ-radiation energy exceeding the threshhold for deuterium. But the intensity of this line is very insignificant; therefore, the amount of Y^{88} required would be ten times as great as that of Na^{24}.

It would seem that the natural isotope ThC"(Tl^{208}) would be a very convenient source for excitation of the reaction $D^2(\gamma, n)H^1$. The ancestors of this isotope, RaTh (Th^{228}) and MsTh$_1$ (Ra^{228}), have half-lives of 1.9 and 6.7 years, respectively. The ratio of standard neutron yields for the sources Na^{24} and MsTh is $\frac{p_{Na^{24}}}{p_{MsTh_1}} \approx 2.9$ [4].

It is easily seen that the use of 1 curie of MsTh$_1$ in our apparatus will permit a counting rate of 1300-1400 imp/minute from a sample of natural water, which will make it possible to carry out isotopic analysis of hydrogen with maximum convenience. We studied the possibility of using a preparation of RaTh for analysis.

Measurements of the latter showed that the photoneutron yield in the reaction (γ, n) corresponds to data published in the literature.

Parallel with this, it was found that the preparation itself generates neutrons, obviously as a result of the the reaction (α, n) taking place under the influence of the natural α-radiation of the preparation on light atomic nuclei $(Z \leq 20)$ [6] present in impurities in the carrier precipitate and in oxygen in the glass of the ampoule and the air inside it.
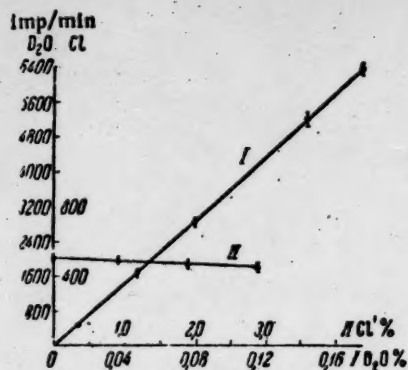
Fig. 2. Graphs of the relation between the counting rate and the D_2O and Cl^- concentrations in water.

Chemical purification of the radiothorium reduced the inherent neutron yield to about one-fifth. Nevertheless, the neutron-emission level reached was high enough to permit consideration of the possible use of natural preparations for isotopic determinations. It is theoretically possible to obtain neutron-free γ-sources on the basis of the thorium series by completely isolating the α-emission from the light elements. This can be achieved, for instance, by preparing metallic thorium with a purity of the order of 99.9-99.99%, enriched in radiothorium, or by preparing a metallic radium-mesothorium mixture from thorium-ore processing wastes. In the latter case the preparation obtained must be kept for several years to permit the accumulation of sufficient ThC* therein. Thus, as a result of preliminary experiments it was shown that it is possible in principle to determine the deuterium concentration in natural waters with high accuracy by the photoneutron method. The slight dependence of the final result of D_2O determination on the variation in the salt composition of the waters opens up the possibility of using this method in oceanology, to analyze layers of ocean water for deuterium without sampling, by the method of (γ, n) logging. On the basis of the simplicity of organization of the analysis and its high productivity, it may be hoped that in the future the photoneutron method of determining deuterium concentration will be used for continuous control of heavy-water production processes in plants manufacturing the latter.

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OPTICAL INVESTIGATION OF THE CONFORMATIONS
OF ACETYLCYCLOHEXENE AND ITS OXIDE

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(Presented by Academician B. A. Arbuzov, July 15, 1959)

Acetylcyclohexene was prepared according to the generally known scheme:
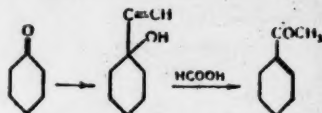
The acetylcyclohexene was oxidized to its oxide with alkaline hydrogen peroxide [1]:
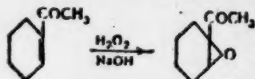
The physical properties of the substances obtained are given in Table 1.

TABLE 1

Physical Properties of Acetylcyclohexene and its Oxide

Compound	B. p. °C/mm Hg	d_4^{20}	n_D^{20}	MR_D	
				found	calc.
Acetylcyclohexene	69—70/8		1,4910	—	—
Acetylcyclohexene oxide	70,5—71,5/8	1,0526	1,4690	37,03	37,10

The Raman spectra of the compounds under investigation were taken in the liquid phase with a domestic Type ISP-51 three-prism spectrograph, provided with a medium camera, and with a Hilger E612 spectrograph, the 4358 A blue line from a mercury lamp being used for excitation*.

Acetylcyclohexene, Δv cm^{-1} 210 (3*), 224 (3*), 267 (0**), 279 (3**), 293 (3**), 299 (0**), 352 (5), 373 (0), 383 (1), 393 (3*), 406 (3*), 446 (3**), 457 (3**), 473 (0), 491 (0), 517 (0), 538 (3 d), 599 (1), 621 (5), 670 (0), 699 (0), 716 (0).

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* Symbols following the intensities: b denotes a broad line, s a sharp line, and d a double line; a number with asterisks denotes lines situated on a common background with adjacent lines which are denoted by the same number of small asterisks.

746 (6), 791 (1°), 804 (1°), 839 (4°°), 850 (5°°), 905 (3°), 924 (2°), 944 (3°),
974 (8), 1009 (0), 1027 (3°), 1034 (3°), 1070 (5°°), 1084 (4°°), 1174 (5s), 1197 (0),
1213 (0), 1237 (4°), 1247 (5°), 1274 (5), 1307 (0), 1347 (4), 1366 (0), 1387 (0),
1427 (10°),1453(4° b), 1639 (10), 1663 (8°), 1672 (8°), 2095 (1), 2109 (1), 2829 (2°),
2864 (5°), 2895 (1°), 2920 (9°), 2933 (9°), 2945 (9°), 2992 (1°°) 3012 (1°°).

Acetylcyclohexene oxide, Δv cm^{-1}: 174 (1°), 189 (1°), 213 (2°°), 225 (2°°),
270 (1°), 280 (3°), 291 (3°), 331 (3°° b, d), 349 (3°° b, d), 361 (1°°), 375 (3°),

390 (1°), 398 (2°), 417 (1), 431 (1), 450 (3°), 460 (1°), 477 (00°°), 490 (2°°),
502 (2°°), 510 (2°), 540 (3), 555 (0), 568 (0), 591 (1°), 606 (2°), 616 (4°),
663 (2°°), 674 (8°°), 707 (0), 721 (1), 745 (2), 773 (6), 821 (5), 841 (5), 858 (6 d),
903 (3°), 914 (5°), 958 (3°°), 975 (3°° b, d), 1023 (1°), 1034 (5°), 1046 (5),
1075 (6°°), 1083 (6°°), 1112 (0), 1139 (3), 1175 (5°), 1189 (3°), 1244 (5°°),
1259 (1°°), 1275 (4°°), 1297 (7°° b, d, 1344 (5 b), 1408 (5°), 1424 (8°), 1438 (8°),
1453 (8°), 1641 (6), 1661 (4°), 1672 (4°), 1703 (9°°), 1713 (7°°), 2096 (3°),
2111 (3°), 2857 (4°°), 2873 (4°°), 2907 (2°°), 2918 (10°°), 2933 (9°°), 2946 (6°°),
2990 (0), 3009 (0). ⸻

The presence of lines in the region of the triple bond (2096, 2111 cm^{-1}) in the spectra of both substances indicates the presence of residues of the original ethynyl compound in the prepared substances. The presence of C = C lines, etc. (see below) in the spectrum of acetylcyclohexene oxide indicates that the oxidation of acetyl-cyclohexene did not go to completion, and the oxidation product is a mixture of acetylcyclohexene and its oxide, but with the latter clearly predominating. Electron diffraction investigations of cyclohexene have shown [2, 3] that the double-bond carbon atoms C_1 and C_2 and the adjoining carbon atoms C_3 and C_6 apparently lie in one (or nearly in one) plane; the molecule has "semi-chairlike" conformations [4] which may be represented schematical-ly in the following form (C—H bonds in the equatorial position are indicated by dotted lines and those in the axial position, by solid lines):
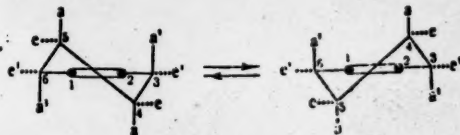
The valences of carbon atoms C_3 and C_6 are quasiequatorial (e') and quasiaxial (a') in character, whereas those of carbon atoms C_4 and C_5 are equatorial (e) and axial (a).

According to the calculations of Beckett, Freeman, and Pitzer [5], the "semi-chairlike" conformation has, from the point of view of energetics, a 2.7 kcal./mole advantage over the "semi-tublike" ones* .

Barton and Hassell's rules [7] with respect to substituted cyclohexenes obviously remain valid [3]. From this it may be concluded that the "semi-chairlike" conformation apparently predominates in acetylcyclohexenes; in this case the acetyl group lies in the plane of atoms $C_1 C_2 C_3 C_6$ or near it:

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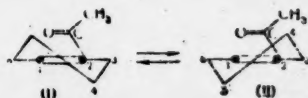
* * Comparison of the calculated distances [6] between the end carbon atoms in the "tub" form of butene \⸺/ (2.88 A), which is an "element" of cyclohexene, and between atoms C_3 and C_6 in the "semi-chair" \/\ (2.94 A) and "semi-tub" /⁻\ (2.56 A) forms shows that the distance between atoms C_3 and C_6 in the "semi-chair" comes closer to the indicated distance in butene, which in turn further indicates that the "semi-chairlike" con-formation predominates in cyclohexene.

There is no reason to deny that the indicated position of this group is also maintained in the conversion transition (I) ⇌ (II).

As the Raman spectrum of acetylcyclohexene shows, the vibration line of the carbonyl group is divided into two: 1663 and 1672 cm^{-1}, whereas the line of the ethylenic bond practically is not divided into a doublet. In the light of what has been set forth above, we are inclined to think that in the given case the cause of the indicated splitting of the vibration line of the carbonyl group is its possible twofold position relative to the ethylenic C = C bond of the ring—the cis-position [(I) ⇌ (II)] and the trans-position [(III) ⇌ (IV)]:
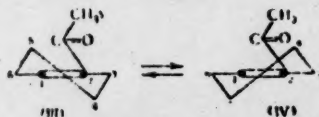
The vibration frequency of the ethylenic bond remains practically unchanged (within the limits of accuracy of its determination with apparatus of the given resolving power). The possible changes in this bond are limited by the skeleton of the six-membered ring of which it is a part. The pulsating vibration frequency of this ring is the same for both (I) ⇌ (II) and (III) ⇌ (IV), and is equal to 746 cm^{-1}*. The carbonyl group, which is free from such restrictions, is characterized by the above-mentioned frequency doublet.

The oxidation of acetylcyclohexene at the double bond leads to the formation of a three-membered oxide

ring , whose C−C bond is simultaneously a C−C bond of the six-membered carbon ring. Electron diffraction data show [9] that the "semi-chairlike" conformation of the six-membered ring is retained in acetyl-cyclohexene oxide. When the indicated position of the acetyl group is maintained, the oxygen atom of the three-membered ring of acetylcyclohexene oxide is apparently located in a plane perpendicular to the plane of atoms $C_1C_2C_3C_6$ or near that position. The optical data obtained by us give substance to these ideas.

As we remarked, the oxidation of acetylcyclohexene was not carried to completion. The presence of a much smaller amount of acetylcyclohexene than of its oxide in the mixture is indicated by the persistence of the following characteristic lines of acetylcyclohexene in the spectrum of this mixture, with sharply reduced intensity: the pulsating vibration frequency of the ring, 746 cm^{-1}; the vibration frequency of the C = C bond in the ring, 1639 cm^{-1}; and the vibration frequency doublet of the carbonyl groups, 1663 and 1672 cm^{-1}. The pulsating vibration line of the six-membered ring of acetylcyclohexene oxide at 773 cm^{-1}, is more intense and higher in frequency than that of the acetylcyclohexene ring. This indicates that 1) acetylcyclohexene oxide actually predominates in the mixture and 2) the formation of the three-membered oxide ring increases the energetic strain of the six-membered ring. The latter circumstance also causes an increase in the vibration frequency of the carbonyl group in acetylcyclohexene oxide relative to that in acetylcyclohexene, the C = O vibration doublet being maintained in this higher-frequency region at 1703 and 1713 cm^{-1}. The presence of this doublet apparently indicates that on oxidation at the double bond of conformations (I) ⇌ (II) and (III) ⇌ (IV), the cis- and trans-positions of the C = O group relative to the C_1−C_2 bond of the oxide ring are maintained; by virtue of the latter affiliation of this bond, it occupies a special place in the six-membered ring. In other words, acetylcyclohexene oxide exists in cis- [(V) ⇌ (VI)] and trans- [(VII) ⇌ (VIII)] conformations:
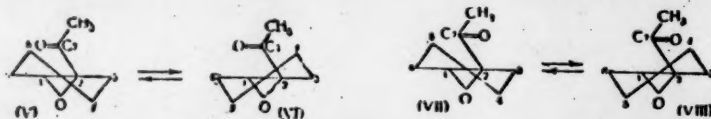
The causes of the appearance of cis- and trans- forms in the two compounds investigated are varied; in the case of acetylcyclohexene such a cause is the interaction of two double bonds (more precisely, the interaction of local magnetic fields generated by the corresponding orbital motion of electrons in the regions of double bonds),

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* The pulsating vibration frequency of cyclohexene is 825 cm^{-1}; in a monosubstituted cyclohexene such as 1-propylcyclohexene-1 it is decreased to 772 cm^{-1} [8]; in the case of acetylcyclohexene it is decreased to 746 cm^{-1}.

whereas for acetylcyclohexene oxide such a cause is slowing of the rotation of the $C = O$ group around the single C_2-C_7 bond (resulting from the creation of a potential barrier as a consequence of the repulsion between the two oxygen atoms on their approach during the rotation of the $C = O$ group and the maintenance of the stated positions of the oxide ring and acetyl group).

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*Original Russian pagination. See C. B. translation.

LOW-TEMPERATURE RADIOLYSIS OF HYDROCARBONS

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Investigation of the radiolysis of hydrocarbons at low temperatures is of interest not only from the point of view of studying the effect of temperature on the process of radiolysis, but also from the point of view of studying the mechanism of radiative-chemical reactions. At low temperatures where the hydrocarbon occurs in the solid phase, the relative importance of the different possible radiolysis routes may be substantially changed. For instance, the quantity of free radicals must decrease, since the possibility of reverse recombination of fragments of a given molecule increases, which must in the first place cause a decrease in the yield of products formed by the breaking of $C-C$ bonds in the hydrocarbon molecule, and also (although to a much lesser degree) a decrease in the yield of products formed by the breaking of $C-H$ bonds. Since diffusion in the solid phase is sharply hindered, fragments obtained from different molecules (with the exception of H atoms) cannot recombine with one another (this relates in general to any bimolecular reactions in the solid phase), and therefore high concentrations of free radicals can accumulate. The hindered character of diffusion in the congealed state even for the H_2 molecule is evident from the fact that there is no hydrogen over the surface of an irradiated congealed hydrocarbon, although it is certainly formed even at low temperature, but not on congealing, since electron paramagnetic resonance data indicate the absence of atomic hydrogen in the congealed irradiated hydrocarbon. At 300°K reactions of the type R + R, generally speaking, may occur either as a result of diffusion of radicals or a chain mechanism of transmission of the free valence. At 77°K, in the solid phase, diffusion is practically excluded and the chain-transmission effect is strongly hindered, so that the radicals obtained on irradiation of congealed hydrocarbons have a practically unlimited lifetime at 77°K. Diffusion of radicals and the chain mechanism of transmission of the free valence are hindered so much at 77°K that the accumulation even of very high concentrations of free radicals does not lead to any appreciable recombination of the latter [1, 2].

TABLE 1

Yields of Hydrogen and Methane (in Moles/100 ev)

Temperature of irradiation, °C	Heptane H_2 yield	Cyclohexane H_2 yield	Isooctane		
			H_2 yield	CH_4 yield	% CH_4 in the methane-hydrogen fraction
300	4.7	5.3	2.2	0.9	29
273	—	4.9	2.0	0.8	29
195	3.9	4.8	1.8	0.5	22
77	3.7	4.7	2.5	0.4	14
55	3.75	—	—	—	—

The possibility of accumulation of radicals depends essentially on their structure and that of the congealed liquid. Thus, for instance, despite the proximity of their melting points, cyclohexane and cetane behave differently; in cyclohexane at 195°K the radical concentration is equal to zero, whereas in cetane it about 40% relative to the concentration obtained by irradiation with the same dose at 77°K.

We investigated the effect of temperature reduction and that of the phase composition on the yield of various radiolysis products.

The method of preparation and irradiation is described in the cited work [1]. The composition of the radiolysis products was determined by adsorption and gas-liquid chromatography; the free-radical concentration was determined with an ÉPR apparatus which gave absorption

TABLE 2

Yield of Individual Hydrocarbons (in Moles/100 ev)

Radiolysis products	300° K	195° K	77° K
Methane	0,15	0,08	0,07
Ethane	0,34	0,34	0,15
Propane	0,42	0,42	0,20
n-Butane	0,46	0,41	0,27
n-Pentane	0,55	0,50	0,36
Total saturated	1,92	1,75	1,05
Ethylene	0,16	0,12	0,07
Propylene	0,12	0,12	0,09
α-Butylene	0,09	0,08	0,07
β-Butylene	0,01	0,00	0,00
Pentene-1	0,09	0,09	0,04
Total unsaturated	0,47	0,41	0,27

spectra directly; IR spectra were taken with an IKS-14 double-beam spectrograph and UV spectra, with an SF-4 spectrum viewer. In the case of irradiation in the congealed state, product analysis (except for e. p. r. spectra) was carried out after freezing.

Data on the hydrogen and methane yields at different temperatures are given in Table 1.

From consideration of Table 1 it is evident that the yield of hydrogen on irradiation of heptane and cyclohexane decreases about 10-15% on transition from room temperature to 195°K, after which further decrease of temperature has no perceptible effect on the yield of H_2* . It should be noted that although cyclohexane solidifies at a higher temperature, heptane still occurs in the liquid state at 195°K, so that some decrease in the H_2 yield should obviously be attributed to the effect of the temperature decrease and not to the solid state. The dependence of the yield of H_2 and CH_4 on temperature in the case of isooctane is especially interesting. The H_2 yield (Table 1) decreases somewhat on transition from room temperature to 195°K, whereas at 77°K, on the contrary, it even increases, while the amount of CH_4 decreases markedly as the temperature falls.

Atomic hydrogen can form H_2 molecules by two routes:

$$H + H \rightarrow H_2, \tag{1}$$

$$H + RH \rightarrow R^{\cdot} + H_2. \tag{2}$$
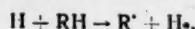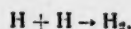
the second reaction having a certain activation energy. Notwithstanding this, by virtue of the enormous difference in the concentrations of H and RH, the bulk of the H_2 must be formed thru reaction (2) at 300°K. At 77°K this reaction is hindered, which should lead to a decrease of up to one-half in the yield of that part of the H_2 obtained by the radical route. In fact, however, the decrease in the total quantity of hydrogen amounts only to about 15%, whereas in the case of isooctane the yield even increases (while the molecular route of H_2 formation, which involves olefin formation, as will be shown below, does not depend on temperature); this is due to two causes: 1) the second reaction is not completely excluded, since the atomic hydrogen formed may be "hot", and 2) the decrease in the yield of fragments from breaking of a C—C bond may lead to partial compensation of the observed H_2 yield, since any increase in the yield of radical fragments will necessarily lead to a decrease in the yield of molecular hydrogen and vice versa, as was especially well manifested in the case of isooctane, where this effect leads not only to compensation of the decrease in the H_2 yield, but also to increase of the latter at 77°K, where the yield of radical fragments is sharply reduced (see the relation between methane yield and temperature, Table 1).

From Table 2, in which are given the yields of individual hydrocarbons from C_1 to C_5, obtained in the radiolysis of heptane at three temperatures, it is evident that the light, saturated radiolysis products, as well as the light, unsaturated ones, are somewhat decreased on transition from room temperature to 195°K, and further that their quantity is further decreased to about 56% at still lower temperatures. The change in the composition and quantity of unsaturated, liquid radiolysis products is shown in Table 3.

At all temperatures (for a dosage of about $2.4 \cdot 10^{21}$ ev), according to the data of IR absorption spectra, trans-olefins, α-olefins, and vinylidene structures are formed.** The formation of trans-olefins and α-olefins does not depend on the temperature within the limits of measurement error; hence it may be assumed that they are formed by a molecular mechanism. The amount of vinylidene structures sharply decreases as the temperature falls, which is probably due to the secondary character of their formation. The ratio of trans-olefins to α-olefins is practically constant at all temperatures and is equal to 3 : 1. Determinations of the total quantity of liquid

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* These data agree qualitatively with Dewhurst's results [3].

** With very large dosages at 300°K ($25-30 \cdot 10^{21}$ ev) there is noted the appearance of trisubstituted, unsaturated structures in a quantity of lower order than that of trans-olefins (oral communication by B. A. Smirnov).

olefins by two independent methods (IR absorption spectra and iodine number determined by the bromine method) agreed well among themselves (Table 3). The mechanism of formation and the temperature dependence of the heavy, unsaturated structures require a special study.

Fig. 1. UV absorption spectra of heptane irradiated at: 1) 273 and 300°, 2) 195°, 3) 77 and 55°K. Dosage $1.8 \cdot 10^{20}$ ev. The figures following the numbers of the curves correspond to radiation yields g in molecules per 100 ev.

The temperature dependence of the yield of diene compounds should be discussed separately, although the diene yield is two or more orders less than the total yield of liquid olefins. Nevertheless, dienes are certainly primary radiative reaction products, as is proved by the linearity of increase of their concentration with respect to the dosage [4]. As the temperature decreases (Fig. 1), the diene yield increases several times. A possible explanation of this interesting fact may be the facilitation at low temperatures of the complex molecular rearrangements which an alkane molecule must undergo to form a diene.

As is evident from Table 4, the amount of the entire heavy residue (compounds $\geq C_{10}$) decreases nearly to two-fifths on transition from 300 to 77°K. As the temperature falls, the percentage of unsaturated compounds in the heavy residue increases. Since bimolecular reactions begin to go at an appreciable rate only at a temperature of the order of the melting point of heptane (177°K), the point of production of the heavy residue (Fig. 2), obtained on irradiation at 77°K, should be referred to a temperature of about 180°K. Then, as shown in Fig. 2, we shall obtain a linear temperature dependence of the yield of heavy residue.

As a result, low-temperature radiolysis of alkanes does not give appreciable quantities of any new products in comparison with radiolysis at 300°K; only a change in the amounts of certain products occurs.

TABLE 3

Summary Quantities of Liquid Olefins (in Moles/Liter)

Temperature of irradiation, °K	trans-Olefins, ν 965 cm^{-1}			α-Olefins, ν 912 cm^{-1}			Vinylidene olefins, ν 888 cm^{-1}			Total olefins			
	total	amt. of heavy	% of heavy	total	amt. of heavy	% of heavy	total	amt. of heavy	% of heavy	according to IR spectral data	According to iodine-number meas.	amt. of heavy	% of heavy
300	0,034	0,0072	21,2	0,007	0,0012	17,1	0,008	0,0015	18,7	0,049	0,051	0,010	20,4
195	0,031	0,0043	13,8	0,007	0,0009	11,4	0,004	0,0009	22,4	0,042	0,041	0,006	14,3
77	0,035	0,0038	10,8	0,009	0,0011	12,2	0,002	0,0010	50,0	0,046	0,045	0,006	13,0

TABLE 4

Temperature of irradiation, °K	Content of heavy residue, wt. %	Mol. wt.	Mol./100 ev	Content of unsaturates in the heavy residue, wt. %
300	1,0	185-202	1.8	29,4
195	0.53	—	0.96	33,2
77	0.41	—	0.74	43,0
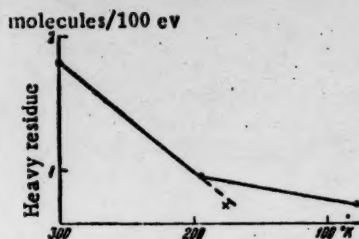
Fig. 2. Dependence of the yield of heavy residue on the temperature of irradiation of heptane.

With regard to the main reaction taking place in the radiolysis of alkanes—hydrogen formation—it may be concluded, on the basis of data on the ratios of products obtained and their temperature dependence, that about 50% of the hydrogen is formed by the molecular route at 300°K, whereas about 60% of the hydrogen is so formed at 77°K, the difference being due to the increase in the contribution of the radical route.

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MICRODETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS THROUGH ELECTRICAL CONDUCTIVITY MEASUREMENT

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The recently-observed trent toward automation of analytical processes is reflected in works on the elementary analysis of organic compounds and, in the first place, carbon and hydrogen determination. These efforts were directed toward achieving automatic regulation of the combustion of the substance under classical microanalytical conditions, i. e., with filled tubes and strictly constant, low oxygen flow rates [1-8]. The completion of the analysis remains gravimetric, and its automation is generally not considered. Such automation, firstly, solves the problem only partially, since the gravimetric completion of the analysis requires just as much of the analyst's time and attention as the combustion, and secondly, does not solve the problem under the most favorable conditions for quantitative oxidation of the substance.
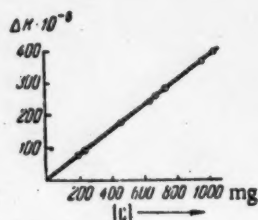
Fig. 1

It appears to us that the correct way to automatic combustion is to create conditions under which complete conversion of the substance to CO_2 and H_2O is attained with a standard procedure in short periods and requires neither regulation of the rate of combustion of the weighed sample nor even observation of it. The basis for establishing such conditions may be pyrolytic combustion according to Korshun and Klimova [9], which, after testing with many thousands of organic compounds, has acquired a reputation as the most universal combustion method. We obtained a substantial increase in the excess of oxygen in pyrolytic combustion by decreasing the weighed sample to about one-fifth. Combustion of a 1-mg sample is carried out in 3-4 minutes; the behavior of the substance is not observed. These conditions are in good accord with the selected nongravimetric completion of analysis. The quantity of CO_2 obtained as a result of combustion, is measured thru the change in electrical conductivity of the absorbent solution. This method of measuring CO_2 is not new and is widely used for the quantitative determination of small concentrations of carbon monoxide in gases [10, 11, 12], carbon in metals and alloys [13, 14, 17], carbon in minerals [15, 16], etc.

In recent years, rapid, automated methods of determining oxygen, carbon, and sulfur in inorganic and organic substances, based on the measurement of electrical conductivity, have been proposed [12-14, 17-19]. The authors of these works, being concerned with the analysis of inorganic items, quite correctly state that the use of this principle is also fruitful in organic analysis, and give a series of examples of the analysis of organic compounds. However, the measurement of hydrogen by change in electrical conductivity has not been worked out hitherto, and the determination of carbon and hydrogen from one weighed sample, completed conductometrically, has not been accomplished until now. The present work is devoted to this problem.

TABLE 1

Substance	Sample wt., mg	C content, %			H content, %		
		calc.	found	differ- ence	calc.	found	differ- ence
Hexachloroethane C_2Cl_6	2,221 2,662	10,14	10,50 10,22	+0,36 +0,08	—	—	—
Oxalic acid $C_2H_2O_4 \cdot 2H_2O$	1,458 1,347	19,05	19,20 19,26	+0,15 +0,21	4,76	4,66 4,57	—0,10 —0,19
Picric acid $C_6H_3N_3O_6$	2,257 1,652	31,45	31,50 31,67	+0,05 +0,22	1,32	1,35 1,30	+0,03 —0,02
Bromobenzoic acid $C_7H_5BrO_2$	0,905 1,220	41,81	42,08 41,61	+0,27 —0,20	2,43	2,53 2,41	+0,10 —0,02
trans-α-Decalone 2,4-dinitrophenyl-hydrazone $C_{16}H_{20}O_4N_4$	1,054 1,125	57,83	57,83 58,01	+0,00 +0,18	6,02	6,14 6,06	+0,12 +0,04
Benzotriazole $C_6H_5N_3$	1,006 0,934	60,50	60,77 60,47	+0,27 —0,03	4,23	4,33 4,24	+0,10 +0,01
1-acetate-12(14)8(13)	1,002		74,67	—0,33		8,21	—0,18
9,11-Dimethylperhydrophenanthrene-dienol-1-one-7 $C_{16}H_{24}O_3$	0,954	75,00	75,10	+0,10	8,31	8,46	+0,15
Naphthalene $C_{10}H_8$	0,710 0,988	93,68	93,38 93,56	—0,30 —0,08	6,32	6,60 6,47	+0,28 +0,15

To determine hydrogen we subject the water, obtained as a result of combustion of the inorganic compound, to decomposition on an incandescent carbon contact layer in a current of pure nitrogen or argon. In this case the oxygen of the water is quantitatively converted to carbon monoxide, which can be determined in various ways. This principle was applied earlier in elementary analysis, to the iodometric determination of carbon and hydrogen [20]. We used it for conductometric completion of analysis.

The essence of the proposed method of carbon and hydrogen determination consists of the following. A weighed sample, about 1 mg, of the organic substance is subjected to rapid pyrolytic combustion in a current of oxygen flowing at a rate of 30-35 ml/minute. The resulting water is frozen out with a mixture of dry ice and acetone, and the remaining carbon dioxide is passed into a cell for measuring electrical conductivity, which contains an absorbent solution. Then the trap containing the frozen-out water is connected into a setup for oxygen determination, the water evaporated and passed over a contact layer of soot, the resulting carbon monoxide oxidized over cupric oxide to CO_2, and the latter then passed into a cell for measuring electrical conductivity.

On the basis of devices for measuring electrical conductivity described in the literature [11, 15, 16], we constructed a cell in which not only a low, but any percentage of carbon in the weighed sample can be determined, owing to an increase in the cell capacity to 55 ml; the absorbent is thoroughly agitated by the gas stream for several minutes, as a result of which the duration of the experiment from the first to the last reading does not exceed 10 minutes. For this cell a linear relation between the amount of carbon and the change in electrical conductivity is maintained up to a carbon content of about 1000 μg in the weighed sample (Fig. 1). Besides the cell, the measuring part of the apparatus includes a ZG-10 sound generator as an alternating-current source, an ÉO-7 oscillograph as a null instrument, an ME-3 capacitor box, and an MTV resistance bridge, all connected in a Wheatstone bridge circuit.

A 0.01 N NaOH or Ba(OH)$_2$ solution is used as CO_2 absorbent. Comparison of the shapes of the curves of resistance change of these absorbents during the experiment shows that at the end of the experiment the resistance is constant in the case of Ba(OH)$_2$, while the curve for NaOH passes thru a maximum, after which it decreases appreciably (Fig. 2). Certain authors also observed this phenomenon and ascribed it to local increase of the CO_3^{2-} concentration in the absorbent solution, which vanishes when complete mixing is achieved [13]. Under our conditions the decrease of resistance is apparently due to hydrolysis of the carbonate ions, as a result of which the quantity of hydroxyl ions in solution increases and the resistance decreases. The absence of such maxima in work with baryta solutions where, owing to the formation of a BaCO$_3$ precipitate, hydrolysis practically does not occur, confirms the correctness of this hypothesis. It should be noted that in 0.005 N NaOH solutions the fall of resistance is considerably greater than in centinormal ones, which are therefore more convenient in use (Fig. 2, 1).
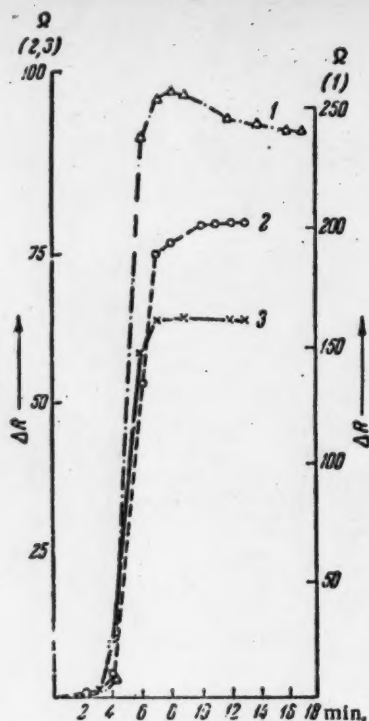
Fig. 2. 1) Absorbent 0.005 N NaOH, quantity of carbon 1028 μg; 2) 0.01 N Ba(OH)$_2$ with 1047 μg; 3) 0.01 N NaOH with 1036 μg.

In Table 1 are given the results of determinations of carbon and hydrogen in organic compounds with varying C content. All analyses gave good agreement of results after two combustions. The mean quadratic error of determination is $+$ 0.14% abs. for C and $+$ 0.01% for hydrogen.

The proposed method of microdetermination of C and H in organic compounds is free to a considerable degree from subjective errors in combustion and in completion of the analysis; this is reflected in the improved reproducibility of results in comparison with gravimetric determinations, despite the small size of the weighed samples. It permits the automation of all stages of the analysis except sampling, and is promising in this sense. The method is also of interest in that it is possible by means of it to study the process of combustion of a substance under varying conditions and to gain some idea of the mechanism of decomposition.

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NEW SYNTHESES OF C-SUBSTITUTED CARBOHYDRATES
AND THEIR DERIVATIVES

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(Presented by Academician A. I. Oparin July 14, 1959)

One of the important methods of determining the structure of carbohydrates is vigorous reduction of the latter to the corresponding hydrocarbons. This reaction was first applied by us to a carbon-substituted monose. As a result of reduction of 1-phenyl-1-desoxyglucose by hydriodic acid, 1-phenylhexane was obtained, which is an additional argument in favor of the structure of C-substituted carbohydrates accepted in the literature.
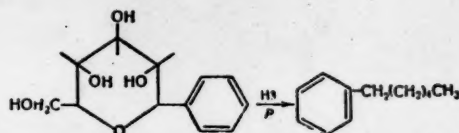
By the reaction of acetobromoglucose with the Norman reagent we prepared, for the first time, a vinylated C-derivative of glucose, which was successfully brominated and mercurated. The previously-obtained 1-(p-amino-phenyl)-1-desoxyacetoglucose [1] was benzoylated and tosylated in the amino group, and also brominated in the benzene nucleus. The first C-substituted derivative of ribose was synthesized: 1-phenyl-1-desoxyacetoribose. Besides, 1-(p-anisyl)-1-desoxymannose and its acetyl derivative were synthesized.

EXPERIMENTAL

Reduction of 1-phenyl-1-desoxyglucose. The initial product was prepared by deacetylation of 1-phenyl-1-desoxyacetoglucose, obtained in the usual manner from phenylmagnesium bromide and acetochloroglucose, with ammonia. The reduction was carried out by the method proposed by O. Schmidt [2] for the reduction of aldonic acids.

Ten g of 1-phenyl-1-desoxyglucose was dissolved in 90 ml of hydriodic acid distilled at 126°, 2.8 g of red phosphorus added, and the mixture refluxed for 12 hours with stirring. After cooling, the liquid was diluted with an equal quantity of water and extracted with ether. The ether extracts were dried over calcium chloride. The dark oil, obtained after driving off the ether, was treated with an excess of sulfuric acid (dilute) and zinc dust in order to reduce the iodo derivatives present. The product was steam distilled and extracted with ether. The ether extract was dried, the ether driven off, and the dark, liquid residue distilled. As a result there was obtained 1.62 g of a clear, slightly yellowish liquid with a pleasant odor. In its properties it was identical with 1-phenylhexane, described in the literature: b. p. 218-220° (literature data, 219-220°); n_D^{20} 1.50 (literature data, n_D^{20} 1.49).

1-Vinyl-1-desoxy-2,3,4,6-tetraacetylglucose. The synthesis was carried out in a three-neck flask provided with a mechanical mercury-seal stirrer and two coils externally cooled by solid carbon dioxide. A 4.83 g quantity (0.18 mole) of magnesium turnings was put into the flask, and there were added 40 ml of tetrahydrofuran freed

from hydroperoxides by boiling with potassium hydroxide, and dried over sodium, a small iodine crystal, 0.5 ml of ethyl bromide, and a few drops of vinyl bromide. The latter was prepared by dropwise addition of a mixture of dibromoethane (150 g) and 500 ml of alcohol to 130 g of potassium hydroxide in 250 ml of water; the vinyl bromide was passed thru a Tishchenko bottle containing water, dried in columns filled with successive layers of calcium chloride and phosphorus pentoxide, and passed down thru a coil connected to the reaction flask intended for preparation of the Norman reagent.

As soon as the reaction began (decolorization of iodine), the stirrer was turned on and vinyl bromide added dropwise until all the magnesium was dissolved, the temperature being maintained near 40°. After all the magnesium was dissolved, the reaction mixture was stirred for 30-40 minutes at 70-80°. On cooling, the Norman reagent formed as a dark-gray mass, after which the coils were replaced by bulb condensers.

A solution of 6.0 g (0.015 mole) of acetobromoglucose in 40 ml of tetrahydrofuran and 60 ml of abs. ether was added dropwise to the Norman reagent during one hour. The mixture was stirred for 3 hours without heating and 5 hours at 60-70°. After this, aqueous ammonium chloride solution, saturated at 0°, was added dropwise to the reaction mass. After stirring for one hour the water layer was separated, washed with ether, and evaporated in a water bath, with a water-jet pump. The dry residue was acetylated with 120 ml of acetic anhydride in the presence of 5 g of anhydrous sodium acetate on heating for 2 hours in a boiling water bath. The solution was poured into ice water and left to stand overnight in order to decompose the acetic anhydride. The acetylated sugar was extracted with ether and the ether extracts washed with sodium bicarbonate solution and water and dried over calcium chloride. The ether was driven off, and there was obtained 2.42 g of a sirup from which, after solution in isopropyl alcohol and precipitation with petroleum ether, 1.72 g of a sirup and 0.278 g of a crystalline product with m. p. 88-89° were isolated. The latter was analyzed.

$$\text{Found \%: C 52,53; H 6,29}$$
$$\text{C}_{16}\text{H}_{22}\text{O}_9.\text{Calculated \%: C 53,59; H 6,14}$$

The substance is described for the first time. Proceeding from the conditions of synthesis, one may represent its structure by the following formula:
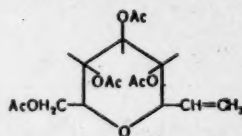
Dibromo derivative of vinylacetoglucose. A 0.1466 g quantity of the above-mentioned vinylacetoglucose was dissolved in 8 ml of carbon tetrachloride, a slight excess of bromine in CCl_4 was added, and the mixture was left to stand for one half hour. The solvent and excess bromine were distilled off in a water bath, the residue extracted with ether, and the ether evaporated. The dibromide was obtained in the form of a caramelized sirup, soluble in benzene, dioxane, ether, and alcohols and insoluble in water and petroleum ether. Yield, nearly quantitative. The product is described for the first time.

$$\text{Found \%: Br 31,23}$$
$$\text{C}_{16}\text{H}_{22}\text{O}_9\text{Br}_2.\text{ Calculated \%: Br 30,86}$$

Mercury derivatives of vinylacetoglucose. A 1.94 g quantity of vinylacetoglucose and 1.85 g of mercuric acetate were dissolved in acetic acid. A mixture of the solutions was heated for 4 hours in a water bath at 70°. The excess acetic acid was distilled off, down to a volume of 25 ml, and the residue poured into 150 ml of water. After slight heating, the precipitate was filtered out, washed with acetic acid and ether, and dried over phosphorus pentoxide. The resulting acetate of the mercury derivative of vinylacetoglucose sintered at 200° and decomposed with evolution of mercury at 270°.

The acetate was converted to the chloride by treatment with saturated sodium chloride solution. The chloride was analyzed for halogen and mercury, the latter being determined radonometrically after the substance was decomposed by heating with nitric acid. The substance is described for the first time; its structure is:

OAc

OAc AcO

AcOH₂C — CH—CH₂HgCl
OAc
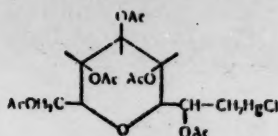
Found %: Cl 5.69; Hg 32.25
$C_{18}H_{25}O_{11}HgCl$. Calculated %: Cl 5.42; Hg 30.71

4-(Acetoglucopyranosyl)benzanilide. A 0.5 g quantity of the previously-prepared 1-(p-aminophenyl)-1-desoxyacetoglucose was dissolved in 5 ml of pyridine, after which 0.2 g of benzoyl chloride was added. The mixture was heated in a flask provided with a reflux condenser for 4 hours in a boiling water bath, after which it was poured into water. The sirup which separated was extracted with chloroform. The chloroform solution was washed with 3 N H_2SO_4, sodium bicarbonate solution, and water and dried over anhydrous sodium sulfate. The chloroform was distilled off and the product recrystallized from abs. ethanol. There was obtained 0.25 g (40% of theory) of a brownish, crystalline substance with m. p. 162-162.5°. The substance is described for the first time.

Found %: N 2.34
$C_{27}H_{29}O_{10}N$. Calculated %: N 2.66

2-Bromo-4-acetoglucopyranosylbenzanilide. A 0.2 g quantity of 4-acetoglucopyranosylbenzanilide was dissolved in glacial acetic acid and 0.8 g of bromine added. After one hour the solution was poured into ice water, the resulting precipitate extracted with ether, and the ether layer washed with sodium bicarbonate solution and water. After drying over sodium sulfate, the ether was distilled off. After recrystallization from abs. ethanol 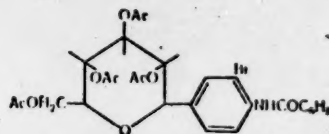there was obtained 0.15 g (65% of theory) of 2-bromo-4-acetoglucopyranoside, m. p. 164-165°. The product was soluble in ether, ethanol, chloroform, and glacial acetic acid. The substance is described for the first time; its structure is:

OAc

OAc AcO
Br
AcOH₂C—
NHCOC₆H₅

Found %: Br 13.17
$C_{27}H_{28}O_{10}NBr$ Calculated %: Br 13.20

Tosylation of 4-acetoglucopyranosylaniline. To 0.2 g of the initial product, dissolved in 5 ml of dry pyridine, was added 0.2 g of toluenesulfonyl chloride. The mixture was heated in a water bath for 4 hours. The cooled mass was poured into water and the resulting precipitate filtered out and recrystallized from abs. ethanol. Yield 0.12 g (44% of theory). Tosylated 4-acetoglucopyranosylaniline was a white, crystalline substance with m. p. 148-148.5°. The substance is described for the first time.

Found %: S 5.03
$C_{27}H_{31}O_{11}NS$. Calculated %: S 5.53

1-(p-Anisyl)-1-desoxytetraacetylmannose. To the ethereal solution of p-anisylmagnesium bromide obtained from 3.93 g (0.16 mole) of p-bromoanisole in 70 ml of abs. ether, 5 g (0.014 mole) of chloroacetomannose in 75 ml of abs. ether was added dropwise, with stirring. The reaction mass was stirred for 5 hours in a hot water bath. Further treatment was carried out in the usual manner. There was obtained 3.25 g (54% of theory) of the acetylated product in the form of a clear, transparent sirup. When this was kept in a desiccator over P_2O_5, a caramel-like solid product was obtained, whose oxidation gave anisic acid. The substance is described for the first time.

Found %: C 57.74; H 6.24
$C_{21}H_{26}O_{10}$. Calculated %: C 57.53; H 5.91

1-(p-Anisyl)-1-desoxymannose. A 0.5 g quantity of 1-(p-anisyl-1-desoxytetraacetylmannose, described directly above, was dissolved in 50 ml of abs. methanol, and the solution was saturated with dry ammonia and

left overnight. After evaporation of the methanol and treatment of the residue with warm ether for removal of acetamide, a solid substance was obtained; after recrystallization from methanol there was obtained 0.23 g (76% of theory) of a cream-colored powder with m. p. 183-184°. The substance is described for the first time.

Found %: C 57.56; H 6.84
$C_{13}H_{18}O_8$. Calculated %: C 57.78; H 6.67

1-Phenyl-1-desoxytriacetylribose. To the ethereal solution of phenylmagnesium bromide obtained from 4.08 g (0.17 mole) of magnesium and 26.69 g (0.17 mole) of bromobenzene, a solution of 5 g (0.017 mole) of α-chlorotriacetylribose in 70 ml of abs. ether was added. The reaction mass was stirred for 5 hours in a hot water bath. Further treatment was carried out as usual. After acetylation there was obtained 1.75 g of a clear sirup (31% of theory), from which 1.15 g of large, transparent crystals of 1-phenyl-1-desoxytriacetylribose, m. p. 94-95°, was isolated. On oxidation of the product with alkaline permanganate, benzoic acid was obtained. The substance is described for the first time.

Found %: C 60.53; H 6.19
$C_{17}H_{20}O_7$. Calculated %: C 60.71; H 5.95

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ABSORPTION SPECTRA OF DERIVATIVES OF
4-NO₂-DIPHENYLAMINE ON THE ROLE OF NH AS AN ISOLATOR
OF OPTICAL CONJUGATION IN DIPHENYLAMINE DERIVATIVES

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In a study of the color of 2,4-dinitro derivatives of diphenylamine (DPA), containing NO_2 groups and a chromophoric donor component [1] $A^2 = OCH_3$, NH_2, NMe_2 in different nuclei, Izmail'skii and Simonov [2, 3] came to the conclusion that in contrast to stilbene derivatives, conjugation which would unite both nuclei into a single system (into a cochromophore [1]) is absent in DPA compounds. The two p-electrons of the $\overset{\times\times}{NH}$ group in DPA are not equivalent to the two π-electrons of the $\overset{\times}{CH}-\overset{\times}{CH}$ group in stilbenes. The color is determined by the system $(NO_2)_2C_6H_3NH-$, which is an "initial primary chromophoric system" of the BKA* type, in which NH is the first donor group. The group A^2 is the second donor group, which modifies the state of the main chromophoric system but does not cause any radical changes in the spectrum. The following hypothesis was advanced: "the mechanism of transmission of electronic perturbations along a chain, interrupted in the middle by a N, S, or O donor atom, is essentially different from that in a continuous K-chain constructed only of CH = CH groups"[2] p. 1660).

These conclusions were confirmed [5-8]. In [8] the author, on the basis of an application of our principle of breaking the structure down into separate components [1, 4, 9], comes to our conclusion: in $O_2NPhNHPh$ derivatives the principal chromophore determining the absorption is $O_2NPhNH-$. The explanation [10] of the bathochromic shift of 4 mμ, observed on introduction of 4'-NH_2 in 4-NO_2PhSPh (I), by conjugation and displacement of the microstructure in the direction of structure (II) is incorrect, since the effect is too insignificant.

(I)   (II)
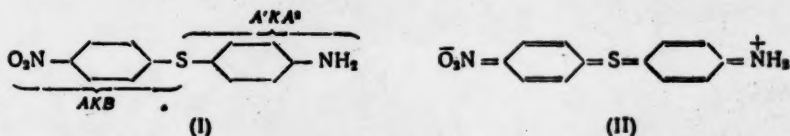
The assumption of structures with a 10-electron shell (II) for S [5b] and N [2] atoms is also incorrect. The absence of conjugation between phenyl and the NO_2Ph system thru S in NO_2PhSPh is also confirmed by the fact that the same λ_{max} (338 mμ) is also observed for NO_2PhSCH_3. There is no conjugation between NO_2 and NH_2 in Ph_2O compounds either, since $O_2NPhOPhNH_2$ has the same maximum as $O_2NPhOPh$, at 300 mμ [10]. On excitation of DPA by light, only those systems, which, as in $C_6H_5\overset{\times\times}{NH}_2$, contain 8 π-electrons (IIIa, IIIb), participate in conjugation and vector displacements. In electron shifts $\Delta+$ always remains on the N atom (IV)

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* The symbols A and B represent electrodotic and electrophilic chromophoric components, and K signifies a conjugated system, e. g., p-C_6H_4 (denoted by Ph) [4].

(IIIa)　　　　　(IIIb)

(IV)
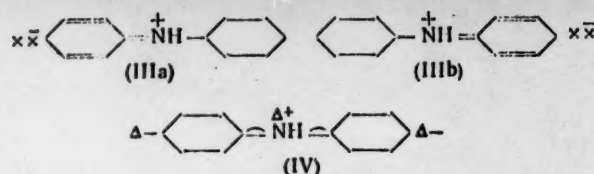
In order to check these conclusions the spectra of DPA derivatives (V) were studied (Table 1). In diagram (V) the geometrical conditions are considered [11], and the directions of vector displacements determining the position of the bands are indicated. NH is the first donor A^1 entering into the BKA system O_2NPhNH which determines the position of the principal long-wave band (system of vector x^I). But NH is also a component of the A^1KA^2 system (system of vector x^{II}) which modifies the state of the principal cochromorphoric BKA system. The A^1KA^2 system must introduce its own band into the spectrum. In the spectrum of (V) we actually find two bands which may be ascribed to a vector displacement of x^I and the displacement of vector x^{II} in the system.
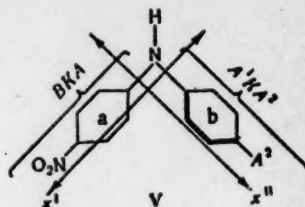
TABLE 1

Spectra of Compounds Having the Structure $O_2N-\langle\ \rangle-NH-\langle\ \rangle-A^2$ (V) in 95% Ethanol, $C = 10^{-4}$

No.	Structure Ph = $-\langle\ \rangle-$ or C_6H_5	Bands of BKA system (vector x^I)			Bands of A^1KA^2 system (vector x^{II})	
		λ^I_{max}	ϵ^I_{max}	$\Delta\lambda$	λ^{II}_{max}	ϵ^I_{max}
1	$O_2NPhNHPh$	395	29220	0	257	13500
2	$O_2NPhNHPhNHCOCH_3$	397	13800	+ 2	274	9820
3	$O_2NPhNHPhOCH_3$	400	25800	+ 5	257	12300
4	$O_2NPhNHPhNH_2$	405	21100	+10	260	13780
5	$O_2NPhNHPhNMe_2$	410	22650	+15	265 (325—340)	19220 (5600)
6	$O_2NPhNMe_2$ [13]	390	19020			
7	$O_2NPhNEt_2$ [13]	400	21550			

The band having λ^I_{max} 395 mμ (A = H, No. 1, Table 1) is actually the bathochromically shifted para-NO_2PhNH_2 band which lies near the band of $p-NO_2PhNMe_2$ (Fig. 1).

Introduction of donors in (V) (A^2 = OCH_3, NH_2) causes only a slight bathochromic shift of band x^I (Fig. 1). In the case of (V) where A^2 = NMe_2 (No. 5, Table 1), the entire band proved to be shifted both bathochromically and hyperchromically relative to that of $O_2NPhNEt_2$ (Fig. 2). The numbers of the curves in Figs. 1 and 2 correspond to the numbers in Table 1. Spectrum 8 in Fig. 2 corresponds to the compound $Me_2NPhNMe$ [12].

The hypothesis, that the λ^{II} bands in the spectra of DPA derivatives (V) (A^2 = 4'-NH_2, 4'-NMe_2, 4'-CH_3CONH) belong to the A^1KA^2 system, was confirmed by the close similarity to the β-band of two-donor chromophoric systems $A^1-C_6H_4-A^2$ containing two N donor atoms in the p-position.

In order to check the hypothesis on the origin of the second band, which we ascribe to the system $A^1-C_6H_4-A^2$ (XI, A^1KA^2), we compared the spectra of the 4'-CH_3CONH-, 4'-NH_2, and 4'-NMe_2 derivatives of DPA (Nos. 2, 4, and 5, Table 1) with the spectra of p-two-donor chromophoric systems containing two N atoms in p-positions. In their spectra we find two bands α and β:

	β- band	α- band
p-$H_2NC_6H_4NMe_2$	256 mμ ($\epsilon=12020$);	323 mμ (ϵ 2239)
p-$Me_2NC_6H_4NMe_2$	264 mμ ($\epsilon=16220$);	318 mμ (ϵ 2455)
$O_2NC_6H_4NHC_6H_4NMe_2$	265 mμ ($\epsilon=19220$);	325—330 mμ (ϵ 5600)
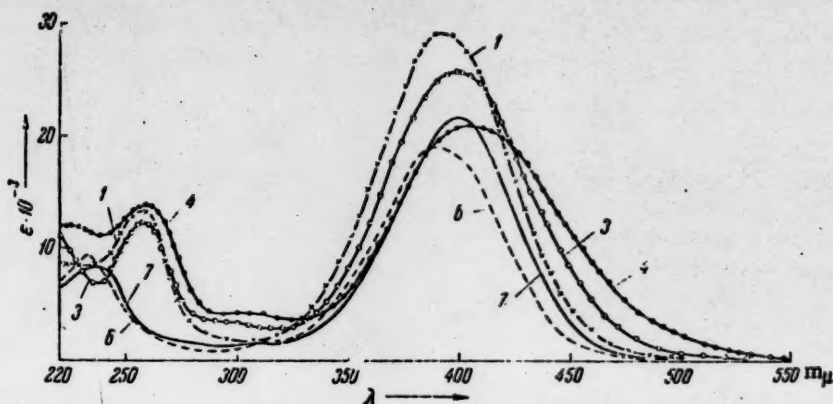
Fig. 1
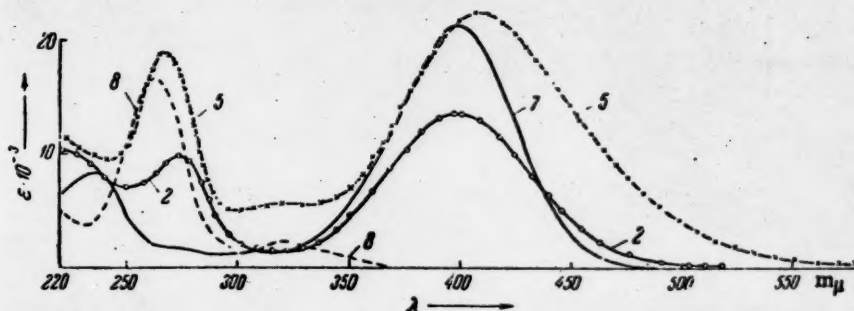
Fig. 2

The A^1KA^2 band for 4'-NMe_2-, 4-NO_2-DPA (No. 5, Table 1) proved to be very near the β-band of para-$Me_2NPhNMe_2$ (TMPP) (Fig. 2, 5 and 8). The presence of still a third band in Curve 5 (Fig. 2) in the 325-340 mμ region, protruding in the form of a curved bulge, is very interesting. We may ascribe this third band to superposition of the α-band of a TMPP-type system: λ_{max} 318 mμ ($\epsilon = 2455$) [12]. Our hypothesis that the second band belongs to the A^1KA^2 system was confirmed.

As could be expected, in the curve of 4'-CH_3CONH, 4'-NO_2-DPA (Fig. 2, 2) λ^I_{max} for the band of the BKA system is shifted hypsochromically relative to the 4'-NMe_2 derivative ($\Delta\lambda = 12$ mμ). The second band (λ^{II}_{max}) lies very close to the band (λ^{II}_{max}) of the NMe_2 derivative (but somewhat shifted bathochromically) and to the β-band of TMPP. The absence in (V) of a single system with conjugation thru NH further confirms the extremely small magnitudes of the shifts in λ_{max} observed on introduction of A^2; when $A^2 = 4'$-OCH_3, 4'-NH_2, or 4'-NMe_2 is introduced, $\Delta\lambda$ only amounts to + 5, + 10, or + 15 mμ, respectively (Table 1). If A^2 entered into conjugation, we would observe values of the order of + 40—80 to + 130 mμ, as is evident from comparison of $\Delta\lambda$ observed on introducing A into O_2NPh (values of $\Delta\lambda$ are +40, +107, and +122 mμ for $O_2NPhOCH_3$, O_2NPhNH_2, and $O_2NPhNMe_2$, respectively) or 4-O_2N-stilbene.

Thus, the present investigation confirmed our earlier conclusions [2] that in DPA and its derivatives (just as in Ph_2S and its derivatives [3, 4]) a single conjugated system of π-electrons with a single excitation vector

along the π-system is absent. In (V) there are two separate BKA and A^1KA^2 systems with their own laws of transition to excited states. We find the bands of these systems in the spectra of (V). These systems "intersecting" at the N atom of the system thus prove to be interconnected, dependent on each other to a certain degree. Conclusions on conjugation, based on the study of chemical reactivity, cannot be accepted as correct [14]. Effects of increase in chemical reactivity are not an accurate criterion of the presence of conjugation, since an increase in chemical reactivity may be caused by inductive influences [1].

Some of the compounds (Table 1, Nos. 1, 3, and 4) had the same m. p. as in the literature. Compound No. 2 had m. p. 224° instead of 22° (apparently a typographical error [15]) and crystallized with one molecule of water.

After drying $C_{14}H_{13}O_3N_3 \cdot H_2O$ at 150° for 3 hours

$$C_{14}H_{13}O_3N_3 \cdot \begin{matrix} \text{Found } \% & \text{N } 15.54; \ 15.46 \\ \text{Calculated } \% & \text{N } 15.50 \end{matrix}$$

No. 5 (Table 1) was synthesized thru the o-sulfonic acid of 4-nitro-4'-dimethylaminodiphenylamine with subsequent hydrolysis (HCl) (yield 72%) and purification of the hydrochloride of the base. M. p. 156°.

$$C_{14}H_{15}O_2N_3 \cdot \begin{matrix} \text{Found } \% & \text{N } 16.63 \\ \text{Calculated } \% & \text{N } 16.35 \end{matrix}$$

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DETERMINATION OF THE SOLUBILITY OF BERYLLIUM OXIDE
IN A LIQUID COPPER-BERYLLIUM ALLOY

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Depending on the preparation method, metallic beryllium contains various amounts of beryllium oxide. According to Sloman's data [1] beryllium forms a eutectic with beryllium oxide containing 0.3% of the oxide. A number of other investigators (for example [2, 3]) denied the possibility of the formation of a eutectic. According to their data, beryllium oxide can only be present in metallic beryllium in the form of inclusions. In an electronographic study of various beryllium samples, Scott and Wilman [4] found that the oxide concentrates mainly at the grain boundaries. At the same time, photographs of the microstructure of compact beryllium, obtained by powder metallurgy [5], clearly show oxide inclusions not only at the grain boundaries, but also inside the grains themselves. According to recent literature data [6], metallic beryllium remelted in vacuum contains 0.1−0.3% of beryllium oxide while powdered beryllium contains 0.8−1.0% of oxide. We undertook an investigation of the solubility of beryllium oxide in a liquid copper-beryllium alloy over the temperature range 1254-1517°. The copper-beryllium alloy contained 2% Be.

EXPERIMENTAL

For determining the solubility of beryllium oxide in the copper-beryllium alloy we prepared a carefully blended mixture of powdered copper, beryllium and beryllium oxide. The amounts of copper and beryllium were calculated to give a 2% beryllium alloy and the amount of beryllium oxide to give a 0.5−1% content on the weight of alloy.

TABLE 1

Temp. °K	BeO content of alloy, %	$N_{BrO} \cdot 10^{-3}$ found	calc. from eq. (1)	Relative error, %
1527	0,039	1,00	0,98	−2,0
1631	0,053	1,32	1,38	+4,5
1752	0,075	2,04	1,96	−3,9
1790	0,084	2,14	2,17	+1,4

The beryllium oxide was obtained by firing beryllium hydroxide at 1100°. The hydroxide was obtained by precipitation with ammonia from twice-recrystallized beryllium nitrate. "Pure" grade copper was used and the beryllium was 99.8% pure. The intimate mixture of these components was briquetted under a pressure of 300 kg/cm². The briquets obtained were fired in vacuum at 800° for 8 hours. The solubility was determined in the special apparatus shown in Fig. 1. Two holes were drilled in the walls of the corundum crucible 1 on an ultrasonic drill and through these was passed a loop of molybdenum wire 2. Into the crucible was placed a briquet in which had previously been drilled a hole for the thermocouple cover. The crucible on the loop was suspended from a section of thin copper wire 3, held between two molybdenum guides 4. The guides were fused into a ground glass cap 5, fitting onto a quartz tube with water-cooled walls. When the cap with the crucible suspended from it was placed onto the quartz tube, the crucible was in the operating zone of the inductor of a high-frequency furnace 7. The cap had openings for a hermetically sealed thermocouple lead 8 and the admission of an inert gas 9. If an electric current was passed through the molybdenum guides, the copper wire connecting them melted and the crucible with the liquid alloy fell into the quenching bath 10 placed at the bottom of the quartz tube. The

quenching fluid used was a silicone oil. In this way it was possible to quench liquid alloys from various temperatures and after the alloy had been kept at constant temperature for various times. Before an experiment the apparatus was pumped out to a pressure of ~$1 \cdot 10^{-6}$ mm Hg. Fusion was carried out in an argon atmosphere at 500-600 mm Hg. The temperature of the alloy was measured with a Pt—Pt/Rh thermocouple. The e.m.f. of the thermocouple was measured with a PP potentiometer. The thermocouple was calibrated under experimental conditions from the melting points of palladium and nickel (by the "wire" method) and from the solidification points of copper and silver. The temperatures were measured with an accuracy of $\pm 1.5°$. The temperature was regulated with an accuracy of $\pm 2.5°$. The thermocouple in a corundum cover was inserted into a hole previously drilled in the briquet and arranged so that it did not impede the normal fall of the crucible on quenching.
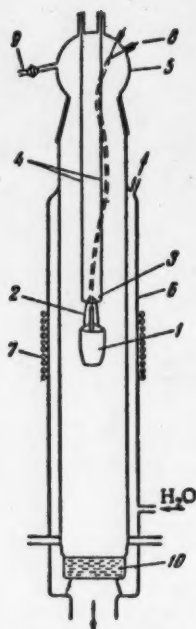
Fig. 1. Plan of apparatus for determining solubility in liquid alloys.
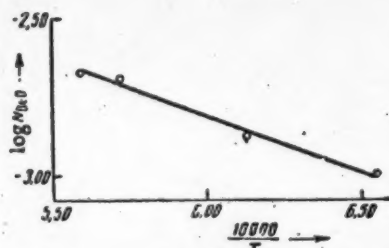
On melting, the copper-beryllium alloy collected in the lower part of the crucible, and a layer of beryllium oxide formed on its surface, as a large excess was present in the starting briquets. The alloy was stirred vigorously as a result of high-frequency currents. Under these conditions equilibrium was established in time between the beryllium oxide dissolved in the alloy and that on the surface of the alloy. The rate at which equilibrium was established was determined by chemical analysis of quenched samples, melted at the same temperature but kept in the molten state for different times. The following results on the establishment of equilibrium were obtained for the Be—CuBe (2%) system at 1254°.

Time kept in a molten state, hours.	0.5	1	1.5	2
Beryllium oxide content of alloy, %	0.010	0.036	0.039	0.039

The beryllium oxide content of the copper-beryllium alloy was determined by the method used for the determination of beryllium oxide in beryllium metal [7]. A sample of alloy was dissolved in a solution of bromine in methyl alcohol. The undissolved residue was beryllium oxide. The latter was dissolved in a mixture of concentrated sulfuric and nitric acids, and determined colorimetrically with Beryllone II [8]. The total beryllium content of the alloy was determined simultaneously. As a rule, the results of determining the total beryllium agreed with the calculated content. Samples from different parts of the ingot were taken for analysis. There was no discrepancy between the analysis results in this case. Table 1 gives the results of determining the solubility of beryllium oxide in a copper-beryllium alloy over the range 1254—1517° C.

At a constant beryllium content, the system beryllium oxide—copper -beryllium alloy is pseudobinary. In this case, if beryllium oxide actually dissolved in the alloy and the solution is ideal, the temperature dependence of solubility should obey Schröder's equation [9]. Figure 2 shows that the temperature dependence of the solubility of beryllium oxide in the copper-beryllium alloy in the coordinates log N_{BeO}—1/T is linear and may be expressed by the equation

$$\log N_{BeO} = -0.6575 - 3591.19/T, \quad (1)$$

where N_{BeO} is the mole fraction of beryllium oxide in the alloy.

Fig. 2. Temperature dependence of the solubility of beryllium oxide in a copper-beryllium alloy.
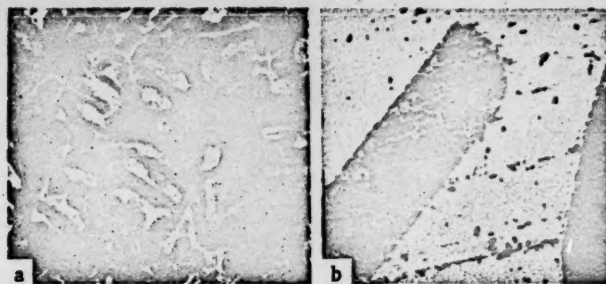
Fig. 3. Microstructure of alloys obtained at 1479°, 80×, (a) and annealed at 800° in vacuum for 15 hours, 600×(b). Etched sections.

The coefficients in equation (1) were found by least squares. From equation (1) it follows that the heat of solution of beryllium oxide in a copper-beryllium alloy containing 2% of beryllium ΔH (1527–1790°) = +16430 cal/mole.

Fig. 3a gives a photograph of the microstructure[*] of an alloy obtained at 1479° and containing 0.075% of BeO. The dendritic structure is clearly seen but no oxide inclusions are visible. Prolonged annealing of solid copper-beryllium alloys saturated with beryllium oxide led to liberation of BeO. Fig. 3b shows a photograph of the microstructure of the same alloy as in Fig. 3a, but annealed at 800° for 15 hours in vacuum. α-Phase grains [10] and beryllium oxide inclusions in various places are clearly visible.

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[*] The etching solutions used were a 10% aqueous solution of cupric chloride and ammonia [10].

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HYDROXYFERROCENE

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Hydroxy derivatives of ferrocene were unknown up to now. Benson and Lindsey [1] synthesized bis(1-hydroxy-3-methylcyclopentadienyl) iron by the reaction of 3-methyl-2-cyclopentenone with sodamide in liquid ammonia and ferrous chloride. Holzbecher [2] showed that in aqueous solutions copper acetate oxidizes phenylboric acid to phenol, and o- and m-nitrophenylboric acids to 2,2'- and 3,3'-dinitrobiphenyl, respectively.

We prepared hydroxyferrocene by two routes through ferrocenyl acetate.

1. Mixing aqueous solutions of ferrocenylboric acid [3] and copper acetate formed ferrocenyl acetate (in 59% yield) and biferrocenyl (21%); when copper propionate was used ferrocenyl propionate and biferrocenyl were formed.

$$F B (OH)_2 + 2Cu (OCOR)_2 + 2H_2O \rightarrow FOCOR + 3RCOOH + Cu_2O + B (OH)_3$$
$$2FB (OH)_2 + 2Cu (OCOR)_2 + 3H_2O \rightarrow F - F + 4RCOOH + Cu_2O + 2B (OH)_3$$
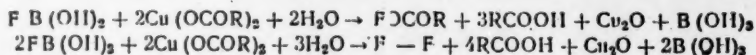
where R is CH_3 or C_2H_5 and F is ferrocenyl, $C_5H_5FeC_5H_4$.

2. Ferrocenyl acetate was obtained by heating bromoferrocene with copper acetate.

As was reported previously [4], a halogen derivative of ferrocene (iodoferrocene) does not react with potassium acetate even when copper is used as a catalyst.

The structure of the ferrocenyl acetate was confirmed by reaction with phenylmagnesium bromide.

$$FOCOCH_3 + 2C_6H_5MgBr \rightarrow FOMgBr + (C_6H_5)_2C - CH_3$$
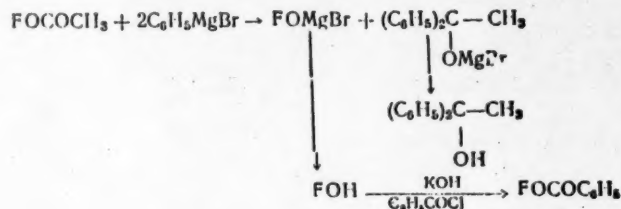
A mixed melting point of the methyldiphenylcarbinol obtained with authentic methyldiphenylcarbinol was not depressed. The hydroxyferrocene formed was benzoylated by the Schotten-Baumann method and ferrocenyl benzoate isolated.

Like phenol, hydroxyferrocene (ferrocenol) was readily isolated from alkaline solutions (after hydrolysis of ferrocenyl acetate in an alkaline medium or by the reaction described above) when carbon dioxide was passed through and it appeared as a yellow crystalline substance which was unstable in air; hydroxyferrocene decomposed when stored in air for a few days or when heated. Hydroxyferrocene could be recrystallized from water (with rapid heating) but it darkened somewhat; it was soluble in ether, alcohols and chloroform. The following derivatives of hydroxyferrocene were obtained: ferrocenyl benzoate, ferrocenyl benzenesulfonate and methoxyferrocene (see Table 1). All the esters were crystalline substances, which were readily soluble in organic solvents.

TABLE 1

	Formula	M.p. °C
Hydroxyferrocene	$C_5H_5FeC_5H_4OH$	166—170 (under nitrogen)
Methoxyferrocene	$C_5H_5FeC_5H_4OCH_3$	39,5—40,5
Ferrocenyl acetate	$C_5H_5FeC_5H_4OCOCH_3$	64,5—66
Ferrocenyl propionate	$C_5H_5FeC_5H_4OCOC_2H_5$	30—31
Ferrocenyl benzoate	$C_5H_5FeC_5H_4OCOC_6H_5$	108,5—109,5
Ferrocenyl benzenesulfonate	$C_5H_5FeC_5H_4OSO_2C_6H_5$	90—90,5

Other properties of hydroxyferrocene are being studied.

EXPERIMENTAL

Ferrocenyl acetate. a) To a hot solution of 2.5 g of ferrocenylboric acid in 250 ml of water was added a hot solution of 4.35 g of copper acetate. A red precipitate formed. After 10 minutes the reaction mixture was cooled and extracted with ether; the ether was filtered free from cuprous oxide and washed with water, 3% KOH solution, and water. After removal of the ether, the residue, which was a mixture of ferrocenyl acetate and biferrocenyl, was dried in a vacuum desiccator over P_2O_5. The ferrocenyl acetate was dissolved with ligroin. The insoluble biferrocenyl was washed again with a small amount of ligroin. We obtained 0.42 g (21% of theoretical) of biferrocenyl; after recrystallization from alcohol the product had decomp. p. 230-232° (capillary introduced into a previously heated metal block.

Evaporation of the ligroin left coarse yellow crystals of ferrocenyl acetate with m. p. 58−62°, somewhat contaminated with biferrocenyl. The yield was 1.56 g (59% of theoretical). After recrystallization from alcohol the substance had m. p. 64.5−66°.

$$\text{Found \%: } C\ 59.16;\ 59.00;\ H\ 4.98;\ 4.87;\ Fe\ 22.80;\ 22.76$$
$$C_{12}H_{12}FeO_2. \text{ Calculated \%: } C\ 59.03;\ H\ 4.96;\ Fe\ 22.88$$

b) An intimate mixture of 0.70 g of bromoferrocene and 2 g of $Cu(OCOCH_3)_2 \cdot 2H_2O$ was heated on an oil bath under nitrogen at 135−140° for 2 hours. The reaction mixture was cooled and ligroin added to it. The ligroin solution was filtered and evaporated. The residual crystals were washed on a filter with cold alcohol. We obtained 0.35 g (55% of theoretical) of ferrocenyl acetate with m. p. 62−65°, which gave a negative halogen test. After recrystallization from alcohol the product had m. p. 65−66.5°. A mixture with the ferrocenyl acetate obtained in the previous experiment melted at 64.5−66°.

Ferrocenyl propionate. Under analogous conditions 0.5 g of ferrocenylboric acid in 60 ml of water and 1.0 g of copper propionate in 40 ml of water yielded 0.30 g of ferrocenyl propionate (53% of theoretical) with m. p. 28−29°; after recrystallization from alcohol (with cooling in dry ice), the product had m. p. 30−31°.

$$\text{Found \%: } C\ 60.40;\ 60.60;\ H\ 5.66;\ 5.69;\ Fe\ 21.84;\ 21.61$$
$$C_{13}H_{14}FeO_2. \text{ Calculated \%: } C\ 60.50;\ H\ 5.47;\ Fe\ 21.64$$

In addition, we obtained 0.08 g (20% of theoretical) of biferrocenyl, with decomp. p. 230−232°.

Hydroxyferrocene. 1. To confirm the structure, ferrocenyl acetate was reacted with phenylmagnesium bromide (in nitrogen atmosphere): to a solution of phenylmagnesium bromide (from 0.7 g of bromobenzene and 0.14 g of magnesium in 10 ml of absolute ether) was added a solution of 0.44 g of ferrocenyl acetate in 5 ml of ether with ice cooling. The reaction mixture was stirred at room temperature for an hour and then decomposed with NH_4Cl solution. The ether layer was washed with a small amount of water and alkali solution. The ether was evaporated and the residual crystals washed with ligroin. We obtained 0.23 g (64% of theoretical) of methyl-diphenylcarbinol with m. p. 78−79°, which had m. p. 79−81° after recrystallization from ligroin. A mixture with authentic methyldiphenylcarbinol melted without depression.

The alkaline extract was filtered, washed with ether, and carbon dioxide passed through it. A yellow precipitate of hydroxyferrocene formed and this was collected, washed with water and dried in a vacuum desiccator over P_2O_5. We obtained 0.22 g (60% of theoretical) of hydroxyferrocene. The hydroxyferrocene could be recrystallized from water (with rapid heating) but it darkened somewhat with this procedure.

$$\text{Found \%: } \quad \text{C } 59.34; \ 59.48; \quad \text{H } 5.06; \ 5.09; \quad \text{Fe } 27.26; \ 27.60$$
$$C_{10}H_{10}FeO. \text{ Calculated \%: } \text{C } 59.45; \quad \text{H } 4.99; \quad \text{Fe } 27.65$$

Hydroxyferrocene decomposed during an attempt to determine the melting point under normal conditions. Hydroxyferrocene was stable in a nitrogen atmosphere and had m. p. 166–170°.

2. Hydrolysis of ferrocenyl acetate. Into a flask fitted with a reflux condenser, a stirrer, and a nitrogen inlet tube were placed 6 ml of 10% KOH, 8 ml of alcohol and 0.40 g of ferrocenyl acetate. The reaction mixture was boiled on a water bath for 50 min. The alcohol was removed, the reaction mixture cooled and the dark brown solution of the potassium salt of hydroxyferrocene obtained was rapidly filtered, diluted to 13 ml and a stream of CO_2 passed in. We obtained 0.29 g (88% of theoretical) of hydroxyferrocene.

Benzoylation of hydroxyferrocene. 1. Hydroxyferrocene (0.095 g) was dissolved in 2 ml of 10% KOH solution; 0.15 ml of benzoyl chloride was added. The mixture was shaken until the smell of benzoyl chloride disappeared. The ferrocenyl benzoate was extracted with ether. The ether was evaporated. We obtained 0.13 g of ferrocenyl benzoate which had m. p. 108.5–109.5° after recrystallization from alcohol.

$$\text{Found \%: } \quad \text{C } 66.79; \ 66.93; \quad \text{H } 4.71; \ 4.79; \quad \text{Fe } 18.27; \ 18.26$$
$$C_{17}H_{14}FeO_2. \text{ Calculated \%: } \text{C } 66.70; \quad \text{H } 4.61; \quad \text{Fe } 18.24$$

2. After removal of the alcohol from the hydrolyzate from 0.30 g of ferrocenyl acetate in 4 ml of 10% KOH and 6 ml of alcohol, 0.5 ml of benzoyl chloride was added with cooling. The reaction mixture was stirred until the smell of benzoyl chloride disappeared. The yellow precipitate was extracted with ether. The ether was washed with 2% NaOH solution and water and evaporated. The residue was washed with cold alcohol. We obtained 0.32 g (85% of theoretical) of ferrocenyl benzoate with m. p. 101–104°. After recrystallization from alcohol the product had m. p. 108.5–109.5°.

Ferrocenyl benzenesulfonate. After removal of the alcohol from the hydrolyzate obtained from 0.30 g of ferrocenyl acetate in 5 ml of 10% KOH and 8 ml of alcohol, 0.5 ml of benzenesulfonyl chloride was added. The reaction mixture was stirred (in a nitrogen atmosphere) for 3 hours and then left overnight. The yellow precipitate was extracted with ether. The ether was washed with 2% NaOH solution and water, and evaporated. The residue was washed with cold alcohol. We obtained 0.38 g (90% of theoretical) of ferrocenyl benzenesulfonate with m. p. 81–84°, which had m. p. 90–90.5° after recrystallization from alcohol.

$$\text{Found \%: } \quad \text{C } 56.06; \ 56.07; \quad \text{H } 4.19; \ 4.16; \quad \text{Fe } 16.53$$
$$C_{16}H_{14}FeSO_3. \text{ Calculated \%: } \text{C } 56.15; \quad \text{H } 4.12; \quad \text{Fe } 16.32$$

Methoxyferrocene. This product was obtained by Freudenberg's method [5], which is used for the synthesis of methyl ethers of phenols. To a solution of 0.30 g of ferrocenyl acetate and 0.5 ml of dimethyl sulfate in 5 ml of methanol was added 1.25 ml of 50% KOH solution. The reaction mixture was heated on a water bath for an hour and then cooled and diluted with water. The methoxyferrocene was extracted with ether. The ether extract was washed with 2% NaOH solution and water; the ether was evaporated. We obtained 0.24 g of methoxyferrocene (90% of theoretical) with m. p. 37–39°. The product was recrystallized from methanol; a solution saturated at 36°, was cooled with an ice–salt mixture. The m. p. was 39.5–40.5°.

$$\text{Found \%: } \quad \text{C } 61.18; \ 61.35; \quad \text{H } 5.81; \ 5.82; \quad \text{Fe } 25.44; \ 25.44$$
$$C_{11}H_{12}FeO. \text{ Calculated \%: } \text{C } 61.14; \quad \text{H } 5.60; \quad \text{Fe } 25.85$$

The substance was readily soluble in organic solvents.

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CATALYTIC HYDROGENATION OF SILICON-CONTAINING
γ-NITRILES AND THE FIBER-FORMING PROPERTIESOF POLYAMIDES
BASED ON THE AMINES OBTAINED

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The catalytic hydrogenation of silicon-containing nitriles has been studied very little. By hydrogenating bis(p-cyanophenyl)-dimethylsilane on Raney nickel, Speck [1] obtained the corresponding diamine in 26.6% yield.

$$(CH_3)_2Si\,(C_6H_4CN)_2 \xrightarrow[Ni]{H_2} (CH_3)_2Si\,(C_6H_4CH_2NH_2)_2.$$
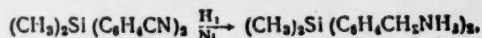
The reaction was carried out in the presence of ammonia at 125–130° and a pressure of 100 atm. Sommer [2] reduced 2-cyanoethyltrimethylsilane with lithium aluminum hydride and obtained γ-aminopropyltrimethylsilane in 82% yield.

$$(CH_3)_3SiCH_2CH_2CN \xrightarrow{LiAlH_4} (CH_3)_3SiCH_2CH_2CH_2NH_2$$
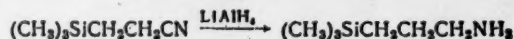
In the present work we studied the hydrogenation of silicon-containing γ-nitriles and the properties of the amines obtained. The latter have not been described in the literature. Polyamides obtained from aliphatic dicarboxylic acids containing a siloxane grouping are known to have rubber-like properties in a number of cases [3]. Condensation of hexamethylenediamine with aromatic dicarboxylic acids containing a siloxane grouping yields fiber-forming polyamides [1]. In both cases the presence of the siloxane grouping in the dicarboxylic acids leads to a fall in the melting point of the polyamides obtained from them. It seemed interesting to investigate the properties of polyamides prepared from the silicon-containing diamines we obtained. On the basis of literature data, it could be assumed that only condensation of these diamines with aromatic acids could lead to the formation of fiber-forming polyamides. Therefore, in our work we prepared polyamides from salts of the diamines and terephthalic acid.

The starting silicon-containing γ-dinitriles, sym-di-(3-cyanopropyl)-tetraalkyldisiloxanes, obtained by hydrolysis of 3-cyanopropyldialkylchlorosilanes [4], had the following constants: $[NC(CH_2)_3-Si(CH_3)_2]_2O$, b. p. 161-162°/2 mm, n_D^{20} 1.4449, d_4^{20} 0.9337; $[NC(CH_2)_3-Si(CH_3)(C_2H_5)]_2O$, b. p. 193°/3 mm, n_D^{20} 1.4513, d_4^{20} 0.9377; $[NC(CH_2)_3-Si(C_2H_5)_2]_2O$, b.p. 193-194°/1 mm, n_D^{20} 1.4592, d_4^{20} 0.9418.

The silicon-containing γ-mononitrile, 3-cyanopropylmethyldimethoxysilane, $NC \cdot CH_2 \cdot CH_2 \cdot CH_2 - Si-$ $-(OCH_3)_2CH_3$, was obtained by the following procedure. Over a period of 1 hour, 40 g of absolute methanol was added with careful stirring and cooling in ice water to a mixture of 120 g of 3-cyanopropylmethyldichlorosilane, $NC \cdot CH_2 \cdot CH_2 \cdot CH_2Si(CH_3)Cl^*$, and 104 g of dry pyridine in 800 ml of dry ether. When the reaction mixture had been stirred for a further 3 hours at room temperature, the ether solution was separated from the pyridine hydrochloride precipitate, the ether evaporated, and the residue vacuum distilled. We obtained 87 g of $NC \cdot CH_2 \cdot CH_2 \cdot$ $\cdot CH_2Si(OCH_3)_2CH_3$ with b. p. 82-83°/3 mm, n_D^{20} 1.4235, d_4^{20} 0.9970; MR_D calc. 45.5, found 45.2. The yield was 77.5%.

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*Obtained by Speier's method [5] from allyl cyanide and methyldichlorosilane in the presence of H_2PtCl_6.

$C_7H_{15}SiO_2N$. Calculated % Si 16.2

The product has not been described in the literature.

The nitriles were hydrogenated in a rotating steel autoclave with a capacity of 0.175 liter into which was loaded nitrile, Raney nickel, and ammonia. Hydrogen was introduced and the electrical heater and rotation mechanism of the autoclave switched on. The reaction was considered complete when the hydrogen pressure in the autoclave no longer fell. The volume of hydrogen absorbed corresponded approximately to that required theoretically. The reaction products were separated from the catalyst by decantation and fractionated in vacuum. The amine fraction was readily distilled on fractionation of the catalyzate and its purity, determined by titration of a sample in 50% alcohol with 0.1 N HCl solution in the presence of a mixed indicator [6], was 97—100% (Table 1). The experimental conditions and yields of the silicon-containing amines obtained are given in Table 1.

TABLE 1

Hydrogenation of Silicon-containing γ-Nitriles on Raney Nickel

γ-Nitrile hydrogenated	Amount, mole	Dinitrile:ammonia, mole	Amount of catalyst, g	Experimental conditions			Amine yield, weight, %	Purity of amine fraction, %
				°C	initial H_2 pressure, atm.	duration, hours		
$NC-(CH_2)_3-Si(CH_3)_2]_2 O$	0.06	1:2	2	75	100	1.5	92	—
$NC-(CH_2)_3-Si(CH_3)(C_2H_5)]_2 O$	0.04	1:2.5	2	75	100	1	87	100
$NC-(CH_2)_3-Si(C_2H_5)_2]_2 O$	0.04	1:4	3	70	100	1.5	70	97.0
$NC-(CH_2)_3-Si(OCH_3)_2 CH_3$	0.8	1:4	3	75	115	1	56	99.3

The constants of the amines and their derivatives are given in Table 2. Thus, we obtained the following sym-di-(4-aminobutyl)-tetraalkyldisiloxanes:

$$\underset{\underset{CH_3}{\overset{CH_3}{|}}}{H_2N(CH_2)_4-\overset{CH_3}{\underset{CH_3}{|}}{Si}-O-\overset{CH_3}{\underset{CH_3}{|}}{Si}-(CH_2)_4NH_2} \tag{I}$$
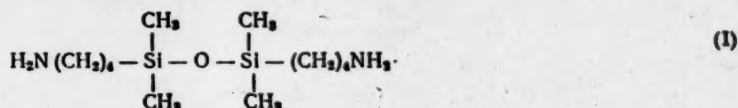
Salt with terephthalic acid:

$C_{12}H_{32}Si_2N_2O.C_6H_6O_2$. Calculated %: N 6.30; Si 12.70

$$H_2N(CH_2)_4-\overset{CH_3}{\underset{C_2H_5}{|}}{Si}-O-\overset{C_2H_5}{\underset{CH_3}{|}}{Si}-(CH_2)_4NH_2 \tag{II}$$
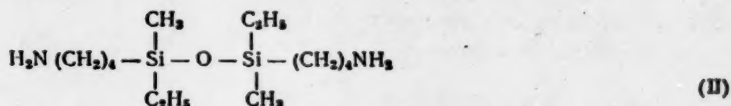
Salt with terephthalic acid:

$C_{14}H_{36}Si_2N_2OC_6H_6O_2$. Calculated %: N 5.90; Si 11.90
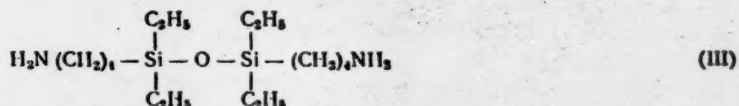
$$H_2N(CH_2)_4-\overset{C_2H_5}{\underset{C_2H_5}{|}}{Si}-O-\overset{C_2H_5}{\underset{C_2H_5}{|}}{Si}-(CH_2)_4NH_2 \tag{III}$$

Salt with terephthalic acid:

As Table 1 shows, I was obtained in 92% yield. The diamine yield fell with an increase in the length of the alkyl side chains at the silicon atom: to 87% for II and to 70% for III. The constants of the amines and their salts in terephthalic acid are given in Table 2. The salts were obtained in the following way: to a 30% solution of diamine in a mixture of alcohol and water (1:1) was added an equimolecular amount of powdered terephthalic acid. The salt was precipitated from the solution obtained with acetone (ratio of 1:10), sucked off, washed with acetone, and dried. The yield was 80-85%.

TABLE 2

Properties of Silicon-containing δ-Amines Obtained by Hydrogenation of the Corresponding γ-Nitriles

Compound	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D		M.p. of terephthalic acid salt, °C
				found	calc.	
[H$_2$N — (CH$_3$)$_4$ — Si (CH$_3$)$_2$]$_2$ O	120—130/4	1.4520	0.8987	82.7	83.1	231
[H$_2$N — (CH$_3$)$_4$ — Si(CH$_3$) (C$_2$H$_5$)]$_2$O	146—147/5	1.4595	0.9023	92.3	91.7	239
[H$_2$N — (CH$_3$)$_4$ — Si (C$_2$H$_5$)$_2$]$_2$ O	156—160/4	1.4652	0.9083	101.3	100.7	242
H$_2$N — (CH$_3$)$_4$ — Si (OCH$_3$)$_2$ CH$_3$	58—60/4	1.4325	0.9430	49.1	48.8	—

To prevent hydrolysis of the methoxyl groups, the silicon-containing mononitrile 3-cyanopropyimethyl-dimethoxysilane was hydrogenated in absolute methanol. We obtained 4-aminobutylmethyldimethoxysilane,

$$H_2N(CH_2)_4 - Si - (OCH_3)_2, \quad \text{b.p.} \quad 58-60°/4 \quad \text{mm}, \quad n_D^{20}1.4325, \quad d_4^{20}0.9430;$$
$$|$$
$$CH_3$$
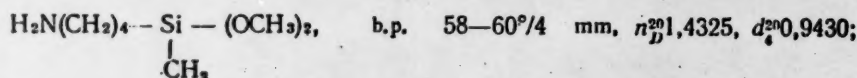
with b.p. 58-60°/4 mm, n_D^{20} 1.4325, d_4^{20} 0.9430; MR_D calc. 49.1, found 48.8. This δ-monoamine with hydrolyzable groups on the silicon atom could be used as a component for preparing alkylsiloxanes containing an amino group in the alkyl chain. All the amines obtained were clear, colorless liquids which were insoluble in water (forming an emulsion) but soluble in 50% alcohol.

TABLE 3

Polycondensation Conditions and Properties of Polyamides Obtained

Amine base used	Preparation conditions	M. p., °C	Specific viscosity of 0.5% solution of polymer in cresol
I	1 hour in a sealed ampoule and 3 hr at 250° in a stream of nitrogen	162—164	0.32
I	The same and 1 hr at 250° and a residual press. of 2 mm	162—164	0.45
II	1 hour in a sealed ampoule and 3 hr at 245° in a stream of nitrogen	147—149	0.32
II	The same at 250°	147—149	0.35
III	The same at 250°	155—158	0.34

Diamine salts which had been reprecipitated twice from aqueous alcohol were used for polycondensation. The polyamides were obtained by thermal polycondensation of the salts prepared, at first in sealed ampoules at 225−230° and then at atmospheric pressure in nitrogen at 245−250° for 3 hours. In some experiments the last stages of the polycondensation were carried out under reduced pressure in order to increase the molecular weight. The polyamides obtained were clear, pale-yellow, horny, elastic resins, indicating their amorphous structure. They were readily soluble in cresol and conc. H_2SO_4 and swelled in hydrochloric and formic acids without dissolving. The polycondensation conditions and properties of the polyamides obtained are given in Table 3. It was established qualitatively that all the polyamides obtained could be spun from melts to form fibers, which could be drawn 300−400% in the cold.

Like other silicon-containing polyamide fibers, their strength was low and they had a low elongation.

The data obtained make it possible to derive certain hypotheses on the effect of both siloxane groupings and side chains on the properties of polyamides. The presence of side substituents is known to produce a fall in the melting point of polyamides due to intermolecular cohesion and a decrease in the capacity to form densely packed chains. The data obtained in the present work confirmed that replacement of methyl radicals at the silicon atom by ethyl radicals leads to a fall in the melting point of the polyamide. The lowest melting point was shown by the polyamide based on the unsymmetrical diamine containing a methyl and an ethyl radical at the silicon atom. The presence of siloxane groups in the main chain of the polyamide, like oxygen atoms, leads to an increase in the flexibility and elasticity of polyamides.

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POLYMERIZATION OF DIENES AND OLEFINS
UNDER THE ACTION OF COBALT OXIDES
AND DIETHYLALUMINUM HALIDES, AND A STUDY
OF THE STRUCTURE OF THE POLYMERS

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Catalytic complexes formed by the interaction of organometallic compounds and titanium halides make it possible to obtain polymers from dienes in which the monomeric units are mainly connected in the 1,4-cis position [1-4]. The use of chromic oxide catalysts (chromic oxide on an aluminosilicate) leads to the formation of crystalline 1,4-trans polymers from dienes [5].

In the present communication we give some data on the polymerization of dienes (butadiene, isoprene, 1,3-pentadiene and 2,3-dimethyl-1,3-butadiene) and olefins (1-butene, styrene and α-methylstyrene) in the presence of cobalt oxide and diethylaluminum chloride or diethylaluminum bromide. The cobalt oxide was prepared from the hydroxide [6] and then activated in a stream of dry air at 300-350° for 5 hours. The product obtained 71-73% of Co, which corresponds to the composition $Co_2O_3-Co_3O_4$. We will subsequently refer to it as cobalt oxide.

Some experiments were with cobalt oxide deposited on an aluminosilicate by impregnating the latter with a 0.1 M solution of cobalt nitrate and then activating it with dry air at 500° for 5 hours. The total cobalt content of the catalyst obtained was 6.7%. The polymerization process was carried out at temperatures of from 0 to 40° with various ratios of cobalt oxide to diethylaluminum halide, whose concentration in the solution was varied from 0.5 to 2.5% of the monomer weight. The components were loaded under conditions which prevented oxygen and moisture from entering the system. The content of 1,2-, 3,4-, and 1,4-cis- and trans-units in the polymers obtained was determined (by infrared spectroscopy)* and the unsaturation was determined by reaction with iodine chloride [7]; in addition, the vitrification point was determined by Marei's method [8] and the molecular weight. The main experimental data are presented in Table 1.

Under the action of the systems consisting of cobalt oxide and diethylaluminum halides, butadiene was polymerized at a considerable rate even at 0°. The use of cobalt oxide on aluminosilicate led to a certain fall in the polymerization rate. The polymers obtained had an unsaturation equal to 97.5-99% of theoretical, indicating that secondary reactions involving the double bonds of the polymer did not occur during polymerization. It is known that in the case of polymerization of butadiene by alkali metals or their organic compounds at about 70°, the double bond content is considerably below theoretical (85-90%). The butadiene polymers had quite a regular microstructure. When cobalt oxide without carrier was used, the amount of 1,2-units in the chain was 5-8% and the total amount of 1,4-units was 95-92% with the bulk of them (about 80%) in the 1,4-cis position. When cobalt oxide on aluminosilicate was used there was some tendency for an increase in the amount of 1,2-units in the chain (Table 1). Due to the high content of 1,4-units in the chain, the polybutadiene obtained had a low vitrification point (about −115°). As the samples obtained began to crystallize even at −20 to −40°, the vitrification point was

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* The authors would like to thank N. V. Mikhailova who plotted the infrared spectra.

TABLE 1

Polymerization of Butadiene and Isoprene in the Presence of Cobalt Oxide and Diethylaluminum Halides

Butadiene

Organometallic compound	Cobalt oxide	Concn. of organoaluminum compound, % of monomer wt.	Molar ratio of Co:AlEt₂Hal	Polymerization temp., °C	Molecular wt. of polymer	Structure of chain			Vitrification point of polymer, °C
						1—2	1—4 trans	1—4 cis	
Diethylaluminum chloride	On aluminosilicate	2,46	1:2,60	20		8	13	79	
		1,63	1:2,02	12		18	18	64	
		0,90	1:0,88	25		9	17	74	—114
		0,66	1:0,92	23		17	15	68	
		0,48	1:0,26	23		10	14	76	—115
	Without carrier	0,49	1:0,28	0		7	18	75	—112
		0,82	1:0,28	20		8	12	80	—112
		0,51	1:2,8	20		7	12	81	—115
		0,51	1:0,28	20	312 000	7	14	79	
Diethylaluminum bromide	Without carrier	0,98	1:0,5	20	355 000	8	14	78	
		0,61	1:3,0	20	1 990 000	5	11	84	
		0,61	1:1,5	20		5	17	78	

Isoprene

Organometallic compound	Cobalt oxide	Concn. of organoaluminum compound, % of monomer wt.	Molar ratio of Co:AlEt₂Hal	Polymerization temp., °C	Structure of chain				Vitrification point of polymer, °C
					1—2	3—4	1—4 trans	1—4 cis	
Diethylaluminum chloride	On aluminosilicate	3,53	1:3,74	40	3	18	58	21	—51
		3,53	1:3,74	40	3	17	62	18	—51
		0,79	1·0,60	25					—51
		0,59	1:0,77	40					—53

• The molecular weight was calculated from the formula $[\eta] = 10.6 \cdot 10^{-4} M^{0.62}$ [9].

determined by Mareĭ's method for samples rapidly supercooled to a temperature below the vitrification point. Isoprene was polymerized more slowly than butadiene and at a higher temperature (about 40°). As in the polymerization of butadiene, the use of cobalt oxide on aluminosilicate led to a fall in the process rate.

The data in Table 1 show that the microstructure of the polyisoprene and the vitrification point were little affected by the organoaluminum compound concentration and the ratio of cobalt oxide to diethylaluminum halide. The presence of quite a large amount of isopropenyl side chains (17-18%) led to a considerable rise in the vitrification point of the polymer. The total content of 1,4-units was about 80% and the bulk of them were in the trans position.

It has already been noted above that isoprene was polymerized at a considerably lower rate than butadiene. A further strong fall in polymerization rate was observed on going to higher dienes. The polymerization rate fell in the series: butadiene > isoprene > 1,3-pentadiene > 2,3-dimethyl-1,3-butadiene.

The vitrification point of poly-2,3-dimethylbutadiene was −16°, which corresponds to that of a polymer in which the units are attached in the 1,4-position.

1-Butene was polymerized at room temperature at a low rate and formed only an amorphous, rubber-like polymer. The characteristic viscosity $[\eta] = 0.377$. Styrene and α-methylstyrene were not polymerized by the given system.

Though we have no data as yet on the nature of the catalytic complex producing polymerization, it should be noted that in contrast to systems consisting of organometallic compounds and titanium tetrachloride, the reaction between cobalt oxides and the organoaluminum compound at temperatures between 0 and 80° is not accompanied by the formation of gaseous hydrocarbons.

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KINETICS OF THE DEHYDROGENATION OF ISOPENTENES

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In previous work [1] a study was made of the kinetics of butene dehydrogenation on a mixed oxide catalyst. The experimental data on the kinetics of butene dehydrogenation could be represented by the equation [2]:

$$\frac{dx}{dt} = K \frac{[A_1]}{[A_1] + z_2[A_2] + z_3[A_3]}. \tag{1}$$

This equation was also shown to be correct for the dehydrogenation of alcohols on an oxide catalyst [3].

The object of the present investigation was to study the kinetics of dehydrogenation of isopentenes. At the present time the catalytic dehydrogenation of isopentenes is of great practical importance as a method of preparing isoprene for rubber synthesis. We previously [4] found conditions for dehydrogenating isopentenes by dilution with steam on an oxide catalyst. We investigated the kinetics of dehydrogenation of isopentenes on the same oxide catalyst over the temperature range 530-580° and also in the presence of water vapor to lower the partial pressure of hydrocarbons. Special experiments showed that dilution of the isopentenes with from 8 to 16 moles of steam had no effect on the reaction rate (Fig. 1). The action was similar to that of inert diluents such as nitrogen or argon. The relative adsorption coefficients z of the reaction products, which appear in equation (1), were found by measuring the dehydrogenation rates of mixtures of the original hydrocarbon with a reaction product (isoprene and hydrogen) under the same conditions as with pure isopentenes.
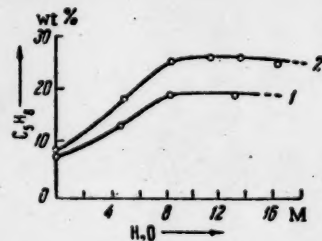
Fig. 1. Effect of the degree of dilution with steam on isoprene formation during the dehydrogenation of isopentenes: 1) At 560°, 2) at 580°.

EXPERIMENTAL

Investigation procedure. The principle of the method was described previously [4]. The experiments were carried out by a flow method. The isopentenes were supplied from steel ampoules of 60 ml capacity, heated at 40° in a thermostat. The rate of isopentene input was regulated with a needle valve, which was very convenient for regulating the flow rate, and controlled with a rheometer. 2 and 4 ml of catalyst were used for the experiments. The degree of dilution with steam was 1 : 11 moles and was kept constant. The reaction products emerging from the furnace passed into a receiver fitted with a reflux condenser, where the steam condensed, and were collected in a trap with a coil, placed in a Dewar vessel and cooled with a mixture of carbon dioxide and acetone. The emergent gas was collected in a gasometer over a saturated solution of sodium chloride. The gas volumes were measured and corrected to NTP. The catalyzate gas was analyzed on a modified Orsat apparatus. The catalyzate was analyzed in the gas phase. For this purpose a sample of catalyzate was evaporated in a stream of nitrogen into a graduated cylindrical gasometer over a saturated solution of sodium chloride and the concentration of hydrocarbons in the mixtures with nitrogen obtained did not exceed

TABLE 1

Dehydrogenation of Isopentenes and Mixtures of Isopentene with Isoprene.   Input
Rate of Mixture 8 Liters (Liquid) per Liter of Catalyst per Hour

Temp., °C	Mixture input in 5 min., ml	Mixture comp., mole, %		Isoprene obtained in 5 min., ml	Gas analysis, vol. %				
		C_5H_{10}	C_5H_8		CO_2	C_3+C_4	C_2H_4	H_2	CH_4
520	384	100	—	35,4	0,6	None	None	98,6	0,8
520	384	77,8	22,2	10,8	1,4	None	None	97,4	1,2
540	384	100	—	56,6	2,2	0,4	None	95,4	2,0
540	384	77,8	22,2	25,1	3,8	0,6	None	92,6	3,0
560	384	100	—	76,6	2,6	0,6	0,4	94,8	2,6
560	384	77,8	22,2	38,3	4,8	0,4	0,2	91,0	3,6
580	384	100	—	101,0	3,2	0,6	0,3	92,5	3,4
580	384	77,8	22,2	56,3	6,6	0,7	0,2	87,6	4,8
600	384	100	—	124,0	4,8	0,6	0,4	89,6	4,6
600	384	77,8	22,2	74,0	7,8	0,4	0,2	86,2	5,2

15-16% to prevent their condensation. The isoprene content was determined with maleic anhydride on a Bush-marin apparatus, the isopentenes by absorption in a solution of mercuric sulfate in sulfuric acid and the isopentane by combustion over copper oxide. The isopentenes for the experiments were obtained by dehydration of isoamyl alcohol over aluminum oxide and purified by distillation on a column of 60 theoretical plates. The fraction with b. p. 31-38°, containing 2-methyl-1-butene and 2-methyl-2-butene, was collected for experiments.

Results of investigation. Experiments with pure isopentenes were carried out at 520-560° at an isopentene imput rate of 8 liters (liquid) per liter of catalyst per hour. The experimental results are given in Table 1. As the data obtained show, the reaction proceeded without appreciable formation of side decomposition products.
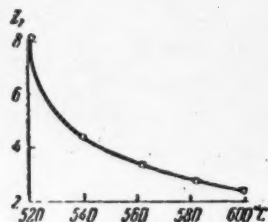
Fig. 2. Temperature dependence of the relative adsorption coefficient of isoprene Z_2.
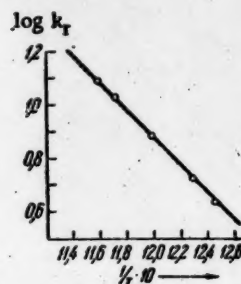
Fig. 3. Relation between the rate constant and the reciprocal absolute temperature.

The hydrogen concentration in the emergent gas was 87.6-98.6%. The reaction rate was determined from the amount of isoprene formed in unit time.

The relative adsorption coefficients of the reaction products, hydrogen and isoprene, which appear in equation (1), were determined kinetically from the fall in reaction rate when the starting material was diluted with a known amount of reaction product. The numerical values of the relative adsorption coefficients were calculated from the formula [2]:

$$Z = \frac{m_0/m - 1}{100/p - 1}.$$

(2)

where m_0 and $\underline{m}$ are the numbers of milliliters of reaction product formed during passage of the pure substance and a mixture with $\underline{p}$ percent of the reacting substance with the reaction product for which $\underline{z}$ is determined. Experiments with mixtures of isopentenes with isoprene were carried out at 530-580° at the same mixture input rate as with pure isopentenes (8 liters of liquid hydrocarbons per liter of catalyst per hour). Mixtures containing 22.2 mole % of isoprene were passed over the catalyst. The data obtained are presented in Table 1. Comparison of data obtained for isopentene—isoprene mixtures with data for isopentenes shows that the degree of conversion of isopentenes into isoprene when mixtures were passed was considerably less than when pure isopentenes were passed. The reaction rate decreased as a result of the retarding effect of added isoprene which was adsorbed more strongly on the active catalyst centers than isopentenes. The relative adsorption coefficient of isoprene Z_2, calculated by formula (2), was 4.46 at 540° and fell to 2.8 with a rise in temperature to 580°. The temperature dependence of Z_2 is shown in Fig. 2. The relative adsorption coefficients of hydrogen, found found from experiments with isopentene—hydrogen mixtures at 560, 580, and 600° and a mixture input rate of 2050 (gas) volumes per volume of catalyst per hour and calculated from formula (2), were found to be equal to 0.8. The hydrogen concentration in the starting mixtures was varied from 25 to 46%. Data for determination of the relative adsorption coefficients of hydrogen are presented in Table 2, which shows that Z_3 had a definite value equal to 0.8 and did not depend on temperature. Thus, isoprene is adsorbed more strongly on the active surface of the catalyst than isopentene and hydrogen is adsorbed almost the same as isopentene.

TABLE 2

Dehydrogenation of Mixtures of Isopentene with Hydrogen. Input Rate of Mixture 2050 Liters (Gas) per Liter of Catalyst per Hour

Temp. °C	Mixture comp., vol. %		Isoprene obtained per liter of mixture, ml	Gas analysis, vol. %				
	C_5H_{10}	H_2		CO_2	C_4	C_5H_4	H_2	CH_4
600	100	—	186	3,4	1,0	0,6	91,8	3,2
600	71,8	28,2	145	2,0	1,0	0,6	94,6	1,8
600	56,0	44,0	111	2,0	1,0	0,6	94,8	1,6
580	100	—	157	2,4	0,8	0,6	93,6	2,6
580	75,4	24,6	124	1,0	0,8	0,2	97,4	0,6
580	52,2	47,8	85,5	0,6	0,6	0,2	98,6	None
560	100	—	128	2,0	0,6	0,4	95,4	1,6
560	77,0	23,0	104	1,0	0,6	None	98,0	0,4
560	54,5	45,4	74,5	0,6	0,6	None	98,8	None

The experimental data obtained were used to find the rate constants of the reaction by equation (1). At temperatures of 530, 540, 560, and 580° the rate constants were equal to 4.3, 5.4, 7.7, and 10.7, respectively. The corresponding activation energy found was 23.3 kcal/mole. The relation between log k_r and the reciprocal absolute temperature is shown in Fig. 3. The points lie on a line and the Arrhenius equation is obeyed. The value of the pre-exponential term log k_0 in the Arrhenius equation was calculated from the formula:

$$\lg k_0 = \frac{\varepsilon}{RT} + \lg k_r. \tag{3}$$

It was found that log k_0 = 7.0.

The values found for the relative adsorption coefficients of isoprene on the catalytically active centers were used in known formulas [3] to calculate the change in free energy, heat content and entropy of adsorption displacement (Table 3).

A comparison of the results obtained for the dehydrogenation of isopentenes to isoprene with data obtained for the dehydrogenation of butenes, whose dehydrogenation kinetics were studied on the same catalyst sample, shows that the dehydrogenation rate of isopentenes is greater than that of butenes. Thus, at 580° the rate constant of

TABLE 3

Adsorption Coefficients, Rate Constants of the Reaction and Thermodynamic Functions of Adsorption Displacement

Temp., °C	k_r, ml/min/ml	Z_2 for isoprene	ΔF, cal		ΔH, kcal/mole	ΔS, cal/°/mole
			C_5H_8	H_2		
530	4,3	5,7	—2410	—		21,7
540	5,4	4,46	—2104			20,8
560	7,7	3,55	—2104	+308	15,3	20,0
580	10,7	2,86	—1780	+315		
590	12,25	2,6	—1637			

isopentene dehydrogenation was found to equal 10.7, while that of butene under the same conditions was 7.26. In all probability the increase in the rate constant of dehydrogenation of isopentenes is produced by the branching of the hydrocarbon chain, as was observed in the dehydrogenation of alcohols of branched structure [3]. The degrees of adsorption of the reaction products, isoprene and butadiene, were also different: butadiene was adsorbed on the active centers of the catalyst more strongly than isoprene, as can be seen from the numerical values of the relative adsorption coefficients.

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KINETICS OF BUTENE DEHYDROGENATION

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As is known [1], butene may be dehydrogenated with dilution by nitrogen or steam or at reduced pressure. All possible variations of the process were worked out by the authors of article [2]. The procedure in which the butene is diluted with steam has a number of advantages over the other methods with respect to the heat supply, simplicity of equipment required, and isolation of the reaction products.

In previous work [3] a study was made of the kinetics of butene dehydrogenation on a chromium catalyst at reduced pressure. A kinetic equation was found which had the form [3]:

$$v_d = k \frac{|C_4 H_8|}{|C_4 H_8| + \Sigma z_n |A_n|},$$ (1)

where v_d is the dehydrogenation rate, $\underline{k}$ is the rate constant and z_n are the relative adsorption coefficients of the substances whose partial pressure is denoted by $[A_n]$.

Shcheglova and Pshezhetskii [4] studied the kinetics of butene dehydrogenation on an aluminochromium catalyst and found that the kinetics were described by an equation close to equation (1), but with other values for the coefficients in the denominator of equation (1) as they were calculated from the ratio of the rate constants of the reactions. The equation had the form [5]:

$$w_2 = \frac{k_2 p_2}{1 + \frac{k_3}{k_4} p_2}.$$ (2)

However, the authors did not consider adsorption and reported that the addition of hydrogen and butadiene had no appreciable effect on the reaction rate. This conclusion is contradicted by our observations. It was found that butadiene is adsorbed on an aluminochromium catalyst and that its relative adsorption coefficient is large and the numerical value increases with a fall in temperature.

The present investigation was devoted to the kinetics of butene dehydrogenation over a mixed oxide catalyst with steam dilution. We found the adsorption coefficients of the reaction products, the rate constants of the reaction over the temperature range 580-620°, and determined the thermodynamic functions of the process: the change in free energy, heat content, and entropy of adsorption displacement from the catalytically active surface of the catalyst.

EXPERIMENTAL

The experiments were carried out by a flow method in the apparatus described previously [6]. The starting hydrocarbons, butene and ethylene, were obtained from the corresponding alcohols by dehydration over aluminum oxide and purified by distillation on a Podbelniak apparatus and on a Davis type column; butadiene was regenerated from tetrachlorobutane with zinc in alcohol; hydrogen was prepared electrolytically. The starting 1-butene

contained about 7% of 2-butene. The catalyzate gas was distilled on a Podbelniak apparatus and analyzed on a modified Orsat apparatus. The butadiene content of the catalyzate was determined with maleic anhydride on a Bushmarin apparatus. The gas volumes were corrected to NTP. Experiments with pure butene and with mixtures of butene and reaction products (hydrogen and butadiene) were carried out with dilution with steam at a ratio of 1:10 moles and at an input rate of 22 volumes per volume of catalyst per hour. 2 ml of catalyst was used for the experiments.
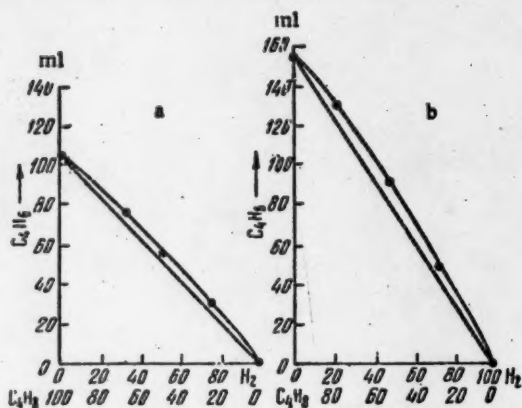
Fig. 1. Curves of butene displacement by hydrogen.

Experiments with mixtures of butene and hydrogen. To determine the relative adsorption coefficients of hydrogen, we measured the rates of dehydrogenation of binary mixtures of butene and hydrogen under the same conditions as for pure butene. The percent hydrogen content of the mixture was varied from 21.8 to 75 mole % (Table 1). Figure 1 shows the rate of formation of butadiene in relation to the mixture composition at 600° (a) and 620° (b). The form of the curves obtained, which lie slightly above the additive line, show that the adsorption coefficients of hydrogen and butene are similar.

Experiments with mixtures of butene and butadiene. We measured the rates of dehydrogenation of binary mixtures of butene and butadiene at 580, 600, and 625° (Table 2). The butadiene content of the mixtures was varied from 26.4 to 92%. These experiments showed

that butadiene was formed and decomposed on the catalyst. The decomposition of butadiene increased with an increase in temperature and an increase in the butadiene content of the mixture, as shown by Fig. 2, 1. To be able to allow for the butadiene decomposition, as in [3], we carried out experiments with mixtures of butadiene and ethylene under the same conditions as with pure butene. Ethylene does not decompose under these conditions and only the decomposition of butadiene could occur. Experiments with butadiene + ethylene showed that as above, butadiene decomposition increased with a rise in temperature and with an increase in the butadiene content of the mixture (Fig. 2, 2). The experimental data was used to find the correction for butadiene decomposi-

TABLE 1

Dehydrogenation of Binary Mixtures of Butene and Hydrogen

Temp., °C	Mixture comp., mole %		Gas analysis, vol %					Amt. of C_4H_8 from 1 liter of mixture, ml
	C_4H_8	H_2	CO_2	C_3+C_4	H_2	C_nH_{2n+2}	C_4H_6	
600	100	—	1,0	86,3	11,5	1,2	9,2	105
	78,2	21,8	0,6	71,8	26,2	1,0	8,1	86
	50,4	49,6	0,4	46,2	50,8	2,0	5,2	54
	25,0	75,0	—	24,0	75,2	0,5	2,9	29,5
625	100	—	2,4	76,2	18,0	2,1	12,4	155
	78,2	21,8	2,2	63,2	31,2	1,2	10,8	131
	51,0	49,0	1,4	42,4	55,2	1,3	7,7	89,5
	24,6	75,4	0,6	22,0	74,1	1,3	4,8	47,5

tion and this was introduced into data obtained with mixtures of butene and butadiene. Curves 2 were subtracted from curve 1 to give curves 3 (Fig. 2) which allow for butadiene decomposition (a—at 600° and b—at 625°).

TABLE 2

Dehydrogenation of Binary Mixtures

Temp., °C	Compn. mole %		Gas analysis, vol. %							Amt. of C_4H_8 from 1 liter of mixture,[*] ml
	C_4H_8	C_4H_6	CO_2	$C_4H_8+C_4H_6$	C_2H_6	H_2	C_nH_{2n+2}	C_4H_6		
Butene — butadiene										
580	100	—	0,6	89,6		9,2	0,6	8,3		82,5
	50,2	49,8	0,6	79,8	0,4	10,6	3,0	45,3		—1,5
600	100	—	1,2	87,0	—	10,4	1,4	9,5		105
	73,6	26,4	3,4	81,4	0,6	11,7	2,6	25,2		37,3
	56,2	43,8	6,0	76,2	0,6	12,8	4,1	35,4		—7,0
	32,0	68,0	7,8	71,5	0,4	13,6	6,1	46,9		—40,5
	8,0	92,0	8,0	73,4	0,4	12,8	3,4	62,1		—122,0
625	100	—	2,4	76,2	—	18,0	2,1	12,1		155
	73,6	26,4	5,6	72,4	0,6	17,4	4,0	23,0		50
	53,2	46,8	6,0	66,2	0,6	19,7	5,1	30,3		—15,5
	32,0	68,0	8,4	70,0	0,6	15,7	4,8	45,2		—69,0
	8,0	92,0	10,0	66,4	0,4	16,2	7,0	57,8		—105,5
Ethylene — butadiene										
580	49,6	50,4	0,6	51,6	45,8	0,6	1,4	48,4		—16
600	75,4	24,6	1,1	28,4	65,0	1,8	1,8	23,1		— 8
	47,4	52,5	2,0	53,4	41,6	1,2	1,8	48,9		—29
	29,8	70,2	4,4	67,0	25,6	0,8	2,2	65,6		—58
625	75,4	24,6	1,6	28,7	64,4	2,2	2,2	23,8		—15
»	47,5	52,5	2,6	51,4	42,2	1,8	1,9	48,0		—45
»	29,8	70,2	4,6	65,8	25,8	1,6	2,2	63,5		—90

[*] The numbers with the minus sign indicate the amount of C_4H_6 decomposed.

DISCUSSION OF RESULTS

The relative adsorption coefficients were calculated from the experimental data on the measurement of the dehydrogenation rates of binary mixtures of butene with butadiene and with hydrogen by means of the formula [3]:

$$z = \left(\frac{m_0}{m} - 1\right) \Big/ \left(\frac{100}{p} - 1\right),$$ (3)

where m_0 and $\underline{m}$ are the numbers of moles of reaction product formed during the passage of the pure starting material and a mixture with $\underline{p}$ percent of the reacting substance with the reaction product for which $\underline{z}$ is determined. The relative adsorption coefficient of butadiene was found to be 4.9 at 580°. With an increase in temperature to

TABLE 3

Rate Constant k_r and Thermodynamic Functions ΔF, ΔH and ΔS

Temp., °C	Rate constant, ml/min per ml of catalyst	z_2	ΔF, cal	ΔH, kcal	ΔS, cal/°/mole
560	5,51	7,5	—3330		22,8
580	7,26	4,9	—2690	18,4	23,0
600	9,3	3,7	—2267		24,7
620	12,13	2,9	—1877		

620°, z_2 decreased to 2.9. The relative adsorption coefficient of hydrogen had a quite definite value of $z_3 = 0.8$, which was independent of temperature over the range 580-620°. The kinetics of butene dehydrogenation were

calculated from the experimental data by means of the general kinetic equation (1). The diluent, steam, does not appear in this equation because, as was shown in preliminary experiments to study the effect of steam on the process, dilution with steam in a ratio of $1:(9-15)$ mole lowers the partial pressure of the hydrocarbon without having any effect on the reaction rate. In this respect dilution with steam is similar to dilution with inert gases such as argon or nitrogen.
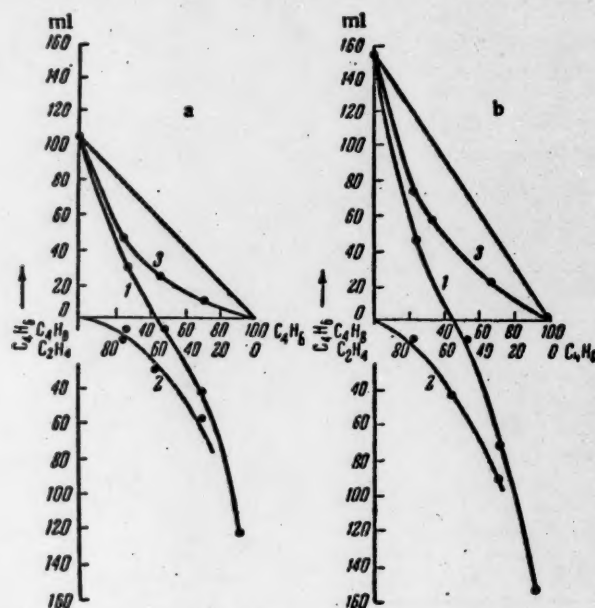

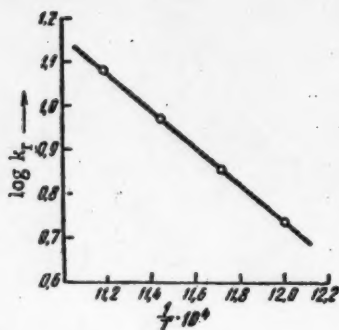Fig. 2. Curves of displacement of butene by butadiene.

Fig. 3. The log k_r, T^{-1} relationship.

The rate constant of the reaction was found to be 7.26 at 580°, 9.3 at 600°, and 12.1 at 620°. There was a linear relation between log k_r and the reciprocal absolute temperature and as Fig. 3 shows, the points lay on a straight line. The activation energy calculated from the reaction rate constant was found to be 19.1 kcal/mole and the pre-exponential term of the Arrhenius equation equaled 5.75.

As we knew the relative adsorption coefficients and thier temperature dependence, we were able to use known formulas [7] to calculate the change in free energy, heat content, and entropy (Table 3) of the adsorption displacement of butene by butadiene from the active centers of the catalyst. The relative adsorption coefficients of butene, butadiene, and hydrogen appearing in equation (1), were in the ratio $1:4.9:0.8$ at 580° and $1:3.7:0.8$ at 600°.

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QUANTITATIVE DETERMINATION
OF AROMATIC ALDEHYDES IN LIGNITES

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The chemical composition of lignites is determined by the nature of the wood and a whole series of external factors (nature of the microflora and conditions under which the wood is buried). However, it should be remembered that the main starting material for the formation of lignites is lignin as the most stable part of the wood. From this point of view it seemed interesting to study the aromatic aldehydes of lignites,which characterize the starting lignin. The generally accepted method of determining the aromatic structural units of lignin is oxidation of the wood with nitrobenzene in an alkaline medium under pressure. Freudenberg et al., [1] and Hibbert et al., [2] developed this method for large samples of wood. For work with small amounts of material, Stone and Blundell [3] proposed a micromethod which made it possible to simplify all the operations considerably and shorten the time for a determination. The authors used paper chromatography for separating the aldehydes and a spectrophotometric method for determining them quantitatively. This method made it possible to work with wood samples of 50-100 mg.

TABLE 1

Species	Sample	Sample No.	Vanillin	p-Hydroxy-benzaldehyde
			mg per g dry weight	
Pinaceae	Peat wood of Pinus silvestris L.	1	27,5	1,12
	Pinuxylon paxii. Kräusel	11	9,55	>1
	The same	17	3,1	Traces
	Pseudolaricixylon firmoides Chudajb.	128	3,24	Traces
Cupressaceae	Cupressinoxylon durum Kräusel	10	4,6	1,7
	Cupressinoxylon hausruckianum Hofm.	47	4,57	2,1
Taxodiaceae	Taxodioxylon taxodii Goth	60	10,05	0,86
	Taxodioxylon anthrotaxoides Chudajb.	49	2,1	Traces
	Taxodioxylon ishikuraense Takamotsu	13	4,66	0,97
	The same	41	2,45	0,78
	Glyptostroboxylon tenerum Conw.	68	4,31	1,27
	The same	88	3,78	>1

In our work we used the method of Stone and Blundell with some changes. Stone and Blundell put the alkaline reaction mixture after nitrobenzene oxidation onto the paper and neutralized it directly on the paper at the spot by laying the paper on a Petri dish with glacial acetic acid. In the work we found that this method of applying the solution and neutralizing it did not give good results. The fact that when the alkaline solution was applied the paper was often broken down at the application point; the spot became very diffuse on neutralization

and this hindered subsequent separation of the aldehydes and made it difficult to obtain sharp spots on the chromatogram. In addition, the alkaline reaction mixture contained a large amount of high-molecular substances which precipitated on acidification and remained on the original spot when the solvent was applied. These substances hampered clean movement of the aldehydes from the starting spot.

We therefore neutralized the alkaline solution in a tube before applying it to the paper. Dilution of the main solution presented no problem as the neutralization of 1 ml of solution required 0.15 ml of glacial acetic acid. A detailed description of the procedure we used is given below.

Alkali-nitrobenzene oxidation. Carefully powdered material was extracted with a mixture of alcohol and benzene (1:1) to remove the tars. A dried, tar-free sample (100 mg) was placed in steel bombs of 4 ml capacity and 2 ml of 8% NaOH and 0.12 ml of nitrobenzene added. The contents were stirred carefully and the bombs tightly closed and placed in an autoclave. The oxidation lasted for 2.5 hours at 160° and 8 atm. At the end of the reaction, the contents of each bomb were transferred to a centrifuge tube and centrifuged. 1 ml of the supernatant liquid was

Fig. 1. Diagram of chromatogram of aromatic aldehydes: 1) Syringaldehyde, 2) p-hydroxy-benzaldehyde, 3) vanillin.

taken and 0.15 ml of glacial acetic acid added. The precipitate was separated by centrifuging. The supernatant liquid was quantitatively (20-100 ml) applied to chromatography paper.

Chromatography. Solvent: ligroin (100-120°)−dibutyl ether−water (6:1:1). The heavy ligroin (100-120°) was obtained by fractional distillation of benzine. A good separation of vanillin, syringaldehyde, and p-hydroxy-benzaldehyde were also obtained by using light ligroin in the same mixture (Fig. 1).

The paper, the base of "crab"parchment, was first washed with butanol. The strips of paper were of a definite form for the best separation of the aldehydes (Fig. 1).

We mainly used the ascending method. The chromatogram was attached at the upper end to the lid of a cylindrical chamber 40 cm high. A crystallizing dish with solvent was placed at the bottom of the chamber. Up to 8 chromatograms were placed in one chamber at the same time. Saturation was achieved in the following way: water was poured into the bottom of the chamber and two small beakers were placed there (one with ligroin and the other with dibutyl ether). Into each beaker was placed the bottom end of a broad strip of filter paper (30 cm long and 10 cm wide), moistened with the corresponding solvent. The separation time was 15-18 hours.

The developer was a 4% EtOH solution of phloroglucinol. After being sprayed with the phloroglucinol solution, the chromatogram was treated with concentrated hydrochloric acid. The position of the aldehydes on the chromatogram is shown in Fig. 1. The actual position of the aldehydes on an undeveloped chromatogram was determined by comparing it with a developed chromatogram from the same chamber. The corresponding section of the chromatogram was cut out, placed in a tube with a ground stopper and 5 ml of alcohol added for extraction. It was also convenient to spray the dried chromatogram with 0.2% alcohol solution of KOH and then the aldehyde spots became visible in ultraviolet light. In this case hot alcohol was used to elute the aldehydes from the paper. After 2-2.5 hours, to 4 ml of extract was added 0.35 ml of a 0.2%alcohol solution of KOH and the optical density of the alkaline solution measured on an SF-4 spectrophotometer at the wavelength characteristic of each aldehyde:concentration was determined from a calibration curve plotted at the characteristic wavelength of each aldehyde: 352 mμ for vanillin, 335 mμ for p-hydroxybenzaldehyde and 371 mμ for syringaldehyde (Fig. 2). These wavelengths correspond to the characteristic ultraviolet absorption maximum of each aldehyde in an alkaline medium. Figure 2 shows the absorption spectra of alcohol solutions of the three aldehydes in an alkaline medium. The effect of the reaction medium on the character of the absorption spectra of p-hydroxyaldehydes and p-hydroxyketones was demonstrated by Englis and Wollermann [4]. The calibration curves were for aldehyde concentrations from 1 to 8 μg per ml.

We investigated 11 samples of lignitized wood of the Tertiary Period from the collection of I. M. Krasheninnikov. The samples were collected from kaolin clays of the western shore of Lake Smolino, close to Chelyabinsk. The samples were kindly given to us by Prof. A. A. Yatsenko-Khmelevskii and R. Khudaiberdyev. A paleobotanical description of the samples was given by R. Khudaiberdyev [5]. For comparison we investigated a sample of buried peat from 15-18 m deep, supplied to us by A. I. Skrigan. Table 1 gives data on the aromatic aldehyde content of the fossil wood after alkali-nitrobenzene oxidation.
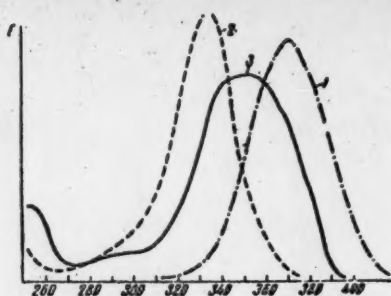
Fig. 2. Absorption spectra of alcohol solutions of aldehydes in an alkaline medium: 1) Syringaldehyde, 2) p-hydroxybenzaldehyde, 3) vanillin.

All the samples investigated were found to contain vanillin and p-hydroxybenzaldehyde. The amount of vanillin varied from 2.1 mg to 10.05 mg per g dry weight of lignite and the p-hydroxybenzaldehyde from 0.78 to 2.1 mg. The total amount of aldehydes in peat wood of Pinus silvestris was several times higher than in lignites. It should be noted that the difference in aldehyde content of different lignites was mainly due to vanillin and the amount of p-hydroxybenzaldehyde was several times less than that of vanillin and varied little in different samples. The vanillin content of lignites was a factor of approximately 10-20 times less than that of similar forms of present-day wood, where the vanillin yield is 25-27% of the lignin [6]. The differences between the p-hydroxybenzaldehyde content of fossil and present-day wood are small.

These investigations of the aromatic aldehyde content of fossil wood again confirm that lignin changes during the conversion of wood to lignites.

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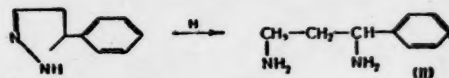
HYDROGENOLYSIS OF PYRAZOLINES

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In 1949 Carter et al. [1] showed that in the catalytic hydrogenation of esters of 3-pyrazolinecarboxylic acids, in which the double carbon—nitrogen bond is conjugated with the carboxyl group, there is rupture of the nitrogen—nitrogen bond with the formation of α,γ-diamino carboxylic acids. There are no data on the catalytic hydrogenation of pyrazolines themselves apart from the work of Diels and Koll [2] who hydrogenated Δ^2-3,5,5-trimethylpyrazoline over colloidal platinum (4-5 hours, 50° and 3 atm.) and isolated as the copper complex a substance to which was assigned the structure Δ^1-3,5,5-trimethylpyrazoline. Our experiments showed that when various pyrazolines were hydrogenated over Raney nickel, hydrogenolysis of the nitrogen—nitrogen bond proceeded smoothly and 1,3-diamines were formed.

Hydrogenolysis of the nitrogen—nitrogen bond apparently occurs first and then reduction of the imine formed, as we were unable to isolate pyrazolidines in any experiment. 1-Alkylpyrazolines were also converted into the corresponding N-alkylated diamines in high yields. The structure of the hydrogenolysis product of 1,3,5,5-tetramethylpyrazoline was proved by synthesis.
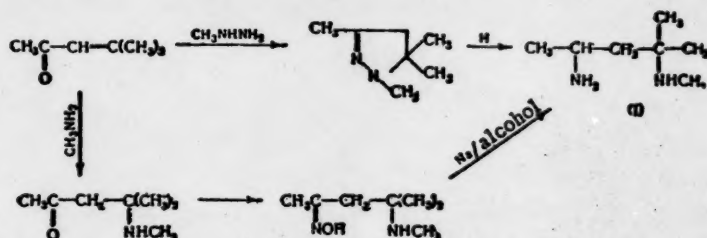
In the case of 1-benzyl-3,5,5-trimethylpyrazoline, we observed elimination of the benzyl group (toluene was isolated), but under analogous conditions, 5-phenylpyrazoline was converted into 1,3-diamino-1-phenylpropane without complications, and though one of the amino groups of this compound is in the "benzyl" position, hydrogenolysis of the carbon—nitrogen bond did not occur.

Thus, hydrogenolysis of pyrazolines is a method of preparing 1,3-diamines, including those with a branched carbon chain, which have hardly been investigated.

Tests carried out by K. S. Shadurskii (Minsk Medical Institute) showed that the diamines synthesized had an anesthetic action and stimulated the cardiovascular system.

EXPERIMENTAL

The hydrogenation was performed in a steel apparatus for continuous hydrogenation, consisting of 4 autoclave tubes of 150 ml capacity. The temperature was kept constant by means of an electronic thermoregulator.

Absolute methyl alcohol was used as the medium and the amount of catalyst was varied from 2 to 7 g per 0.1 mole of pyrazoline. The process was stopped when the absorption of hydrogen ceased. The catalyst was then removed from the reaction mixture by filtration, the alcohol removed, and the residue vacuum distilled in a stream of nitrogen.

Thus, for example, into the autoclave was loaded 16.8 g of 3,5,5-trimethylpyrazoline, 5 g of Raney nickel and 50 ml of absolute methanol. Hydrogenation continued for 6 hours at 6 atm and 100°. Processing as described above yielded 10.6 g (61%) of 2,4-diamino-2-methylpentane with b. p. 70-71.5° (30 mm), n_D^{20} 1.4397, d_4^{20} 0.8366, MR_D calc. 36.58; found 36.75. Literature data [3]: b. p. 36-41° (12 mm).

The dipicrate was prepared in absolute ether and had m. p. 245-246° (with decomposition, from alcohol).

$$C_6H_{16}N_2 \cdot 2C_6H_3N_3O_7.$$
Found %: C 37.73, 37.71; H 4.41, 4.32; N 20.00, 19.85
Calculated %: C 37.64; H 3.86; N 19.50

The diacetyl derivative had m. p. 160.5-161.5° (from alcohol).

$$C_{10}H_{20}N_2O_2.$$
Found %: C 60.30, 60.19; H 10.06, 10.08
Calculated %: C 59.99; H 10.06

The dibenzoyl derivative had m. p. 151-152° (from alcohol).

$$C_{20}H_{24}N_2O_2.$$
Found %: C 73.71, 73.77; H 7.68, 7.54
Calculated %: C 74.05; H 7.46

The following diamines were prepared analogously:

2-Methylamino-4-amino-2-methylpentane (I). (I) was obtained from 11.7 g of 1,3,5,5-tetramethylpyrazoline (10 hours, 100-140 atm). The yield was 28%. b. p. 84-85° (70 mm), n_D^{20} 1.4422, d_4^{20} 0.8370, MR_D calc 41.19, found 41.55. Literature data [4]: b. p. 166-167°.

$$C_7H_{18}N_2.$$
Found %: C 64.05, 63.83; H 13.74, 13.54
Calculated %: C 64.56; H 13.04

The dipicrate had m. p. 187-187.5° (from absolute alcohol).

$$C_7H_{18}N_2 \cdot 2C_6H_3N_3O_7.$$
Found %: C 39.07, 38.89; H 4.13, 4.19; N 19.34, 19.30
Calculated %: C 38.77; H 4.11; N 19.06

2-Propylamino-4-amino-2-methylpentane. This compound was obtained from 46.2 g of 1-propyl-3,5,5-trimethylpyrazoline (10 hours, 80-100 atm) in a yield of 43%; it had b. p. 67-72° (11 mm), n_D^{20} 1.4481, d_4^{20} 0.8427, MR_D calc. 50.27, found 50.78.

$$C_9H_{22}N_2.$$
Found %: C 68.08, 68.24; H 13.03, 13.14
Calculated %: C 68.28; H 14.01

The dipicrate had m. p. 187-187.5° (from alcohol).

$$C_9H_{22}N_2 \cdot 2C_6H_3N_3O_7.$$
Found %: C 40.82, 41.02; H 4.62, 4.58
Calculated %: C 40.91; H 4.58

3,5-Diamino-3-methylheptane. This was obtained from 21 g of 3,5-diethyl-5-methylpyrazoline (5 hours, 70-80 atm) in a yield of 47%; the b. p. was 75-75.5° (10 mm), n_D^{20} 1.4529, d_4^{20} 0.8533, MR_D calc. 45.68, found 45.98.

$$C_8H_{20}N_2.$$
Found %: C 66.47, 66.77; H 13.99, 13.83
Calculated %: C 66.60; H 13.98

The dipicrate had m. p. 234-235.5° (with decomposition, from alcohol).

$$C_8H_{20}N_2 \cdot 2C_6H_3N_3O_7.$$
Found %: C 40.41, 40.18; H 4.44, 4.44
Calculated %: C 39.83; H 4.34

1,3-Diamino-2-ethylhexane. This was obtained from 14 g of 4-ethyl-5-propylpyrazoline (5 hours, 100 atm) in a yield of 83.5%; it had b. p. 99-100° (17 mm), n_D^{20} 1.4578, d_4^{20} 0.8629, MR_D calc. 45.60, found 45.98.

$$\text{Found \%} \quad C\ 66.71,\ 66.79;\ H\ 13.82,\ 13.85$$
$$C_8H_{20}N_2.\ \text{Calculated \%:}\ C\ 66.60;\qquad H\ 13.97$$

The dipicrate had m. p. 204-205° (from alcohol).

$$\text{Found \%:} \quad C\ 40.15,\ 40.01;\ H\ 4.54,\ 4.48$$
$$C_8H_{20}N_2 \cdot 2C_6H_3N_3O_7.\ \text{Calculated \%:}\ C\ 39.87;\qquad H\ 4.34$$

1,3-Diamino-5-methyl-2-isopropylhexane was obtained from 25.2 g of 4-isopropyl-5-isobutylpyrazoline (6 hours, 100 atm) in 48% yield; it had b. p. 104-106° (13 mm), n_D^{20} 1.4559, d_4^{20} 0.8542, MR_D calc. 54.81, found 55.22.

$$\text{Found \%:C}\ 70.08,\ 69.65;\ H\ 13.86,\ 13.84$$
$$C_{10}H_{24}N_2.\ \text{Calculated \%:C}\ 69.69;\qquad H\ 14.03$$

1,3-Diamino-2,2,4-trimethylpentane was obtained from 11.5 g of 4,4-dimethyl-5-isopropylpyrazoline (4 hours, 100 atm) in 68.5% yield; it had b. p. 93.5-94° (25 mm), n_D^{20} 1.4591, d_4^{20} 0.8737, MR_D calc. 45.48, found 45.99.

The dipicrate had m. p. 188-189° (from alcohol).

$$\text{Found \%:} \quad N\ 18.23;\ 18.47$$
$$C_8H_{20}N_2 \cdot 2C_6H_3N_3O_7.\ \text{Calculated \%:}\quad N\ 18.69$$

1,3-Diamino-1-phenylpropane (II) was obtained from 22.9 g of 5-phenylpyrazoline (6 hours, 100 atm); we obtained 13.4 g of diamine (II) (59.2% yield) with b. p. 138-141° (21 mm), n_D^{20} 1.5429, d_4^{20} 1.0136, MR_D calc. 45.72, found 47.18.

$$\text{Found \%:C}\ 71.70,\ 71.98;\ H\ 9.71,\ 9.66;\ N\ 18.15,\ 18.14$$
$$C_9H_{14}N_2.\ \text{Calculated \%:}\ C\ 71.95;\qquad H\ 9.39;\qquad N\ 18.65$$

For the synthesis of diamine (I), to 98 g of mesityl oxide and 68 g of a 33% solution of methylamine hydrochloride was added 40 g of solid NaOH. The mixture was shaken until the oily layer disappeared. The unreacted ketone was extracted with ether and to the aqueous residue was added 70 g of hydroxylamine hydrochloride and then, with cooling, 40 g of NaOH. After 12 hours (at room temperature) the reaction mixture was saturated with potassium carbonate and the liberated oil extracted with ether, dried with potassium carbonate, and distilled. We obtained 55 g (38%) of the oxime of 2-methylamino-2-methyl-4-pentanol with b. p. 133° (11 mm) and m. p. 58°; the benzoyl derivative had m. p. 102° (from alcohol), which agree with literature data [5]. To a solution of 3 g of the oxime obtained in 50 ml of absolute ethyl alcohol was added 5.6 g of metallic sodium. When reduction was complete, the diamine was steam distilled and the distillate collected in HCl. The distillate was then evaporated, decomposed with a concentrated aqueous solution of NaOH and extracted in a liquid extractor. A picrate was prepared from the dry ether solution and after two recrystallizations from alcohol this had m. p. 186° and did not depress the melting point of the dipicrate of diamine (I).

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SYNTHESIS OF A CONJUGATED DINITRODIENE

V. V. Perekalin and O. M. Lerner

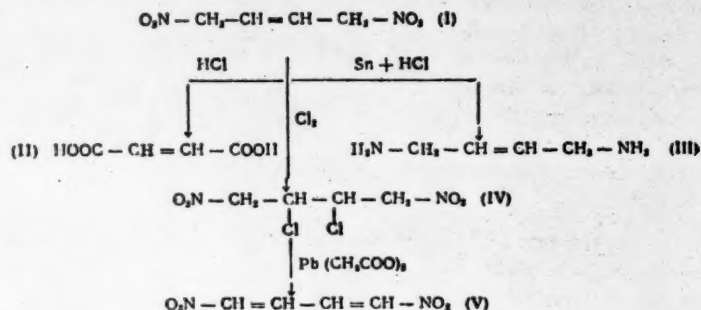(Presented by Academician M. I. Kabachnik, July 11, 1959)

No unsaturated aliphatic nitro compounds containing two conjugated nitrovinyl groups, have been described in the literature. An investigation of the structure and reactivity of such dinitrodienes is of interest as there has been little study of conjugated dienes with two extreme electrophilic groups [1]. For this purpose we synthesized the simplest dinitrodiolefin, 1,4-dinitro-1,3-butadiene (V) from 1,4-dinitro-2-butene (I).

There are no suitable instructions in the literature for a single method of preparing 1,4-dinitrobutene by the addition of nitrogen tetroxide to butadiene [2-5]. It was found that the most important condition for successful nitration was the rapid addition of nitrogen tetroxide to butadiene and the introduction of a crystalline seed of (I). For confirmation of the structure, 1,4-dinitro-2-butene was converted into fumaric acid (II) by acid hydrolysis; this provided a simple method of preparing fumaric acid and hence, maleic anhydride [6].

Contrary to literature data [5], reduction of (I) with tin and hydrochloric acid yielded 1,4-diamino-2-butene (III) and not 1,4-diaminobutane.

In the presence of traces of iodine, (I) slowly added chlorine and was converted to 2,3-dichloro-1,4-dinitrobutane (IV), which was very unstable to alkalis and organic bases.

According to Raman spectral data, in contrast to nitroallene, the double bond in 1,4-dinitro-2-butene participates in the conjugation with the nitro groups [7].

$$O_2N - CH_2 - CH = CH - CH_2 - NO_2 \quad (I)$$

HCl   Cl$_2$ Sn + HCl

(II) HOOC — CH = CH — COOH $H_2N - CH_2 - CH = CH - CH_2 - NH_2$ (III)

$$O_2N - CH_2 - CH - CH - CH_2 - NO_2 \quad (IV)$$
Cl   Cl

Pb (CH$_3$COO)$_2$

$$O_2N - CH = CH - CH = CH - NO_2 \quad (V)$$

The action of lead acetate on (IV) in glacial acetic acid eliminated the elements of hydrogen chloride and formed 1,4-dinitro-1,3-butadiene (V). This synthesis is apparently the first example of the use of lead acetate to convert 1,2-halonitroalkanes to unsaturated nitro compounds. (V) was found to be a very stable compound; it did not undergo diene synthesis, did not react like mononitroolefins with substances with active hydrogen atoms in methylene groups and was slowly brominated to form the dibromide. The intensity of the double bond band in the Raman spectrum of (V) (Table 1) was approximately one order greater than that in mononitroolefins, indicating the presence of a conjugated system in it [7].

TABLE 1

Intensities (on an Arbitrary Scale) and Frequencies (in cm^{-1}) of the Double-Bond Lines in the Raman Spectrum of Some Nitroalkenes

Substance	$-C=C-$ oscillation intensity	$-C=C-$ oscillation frequency
$CH_2 = CHCH_2 - NO_2$	23	1580
$O_2N-CH_2-CH=CHCH_2-NO_2$	80	1660
$(CH_3)_2CH_2CH = CH-- NO_2$	187	1650
$O_2N-CH=CH-CH=CH--NO_2$	2000	1628

Note. The intensities of Raman spectral bands (lines), which change sharply in relation to conjugation, can be used to evaluate the latter. The Raman spectra were examined by Ya. S. Bobovich.

1,4-Dinitro-2-butene (I). [4]. Into a three-necked flask of 250 ml capacity, fitted with a stirrer with a glass plunger seal, a thermometer, and a dropping funnel with a cooling jacket, was placed 100 ml of dry ether. This was cooled to $-10°$ (with a mixture of dry ice and kerosene) and 30 ml (0.36 mole) of butadiene and then 0.2-0.3 g of crystalline 1,4-dinitro-2-butene introduced. With vigorous stirring at $-35°$, a solution of 29 g (0.31 mole) of nitrogen tetroxide in 50 ml of dry ether at $-15--20°$ was added to the solution obtained in such a way that the temperature of the reaction mass did not exceed $-30°$. The time for adding the nitrogen tetroxide had to be as short as possible; usually it did not exceed 20-30 minutes.

The mass was then stirred for a further 5-10 minutes and the precipitated solid product collected by filtration and washed with a small amount of cold ether. The yield of crude product was 16.4 g, i. e., 36% of theoretical, calculated on the nitrogen tetroxide.

1,4-Dinitro-2-butene had m. p. 59-60° (yellow crystals from ethanol with concentrated hydrochloric acid added) and was readily soluble in acetone, dioxane, glacial acetic acid, and chloroform, and difficultly soluble in ether and ethanol. The yield of purified product was 12.2 g, i.e. 27% of theoretical.

$$\text{Found \% } \quad N \ 19.46, \ 19.53$$
$$C_4H_6N_2O_4. \text{ Calculated \% } \quad N \ 19.18$$

Fumaric acid (II). A mixture of 2.92 g (0.02 mole) 1,4-dinitro-2-butene and 20-30 ml of dilute HCl(1:1) was boiled with vigorous stirring for 2-3 hours, a small amount of activated charcoal added and the hot solution filtered. The snow-white crystals which separated when the filtrate was cooled were collected and washed with a small amount of ice water. The product was identified as fumaric acid. The yield was 1.2-1.5 g.

1,4-Diamino-2-butene (III). Into a three-necked flask was placed 35 ml of concentrated HCl (d = 1.19) and then, over a period of 10-15 min, 15 g of electrolytically precipitated tin was added in portions with the simultaneous introduction from a dropping funnel of a warm solution of 1.46 g (0.01 mole) of dinitrobutene (I) in 6-8 ml of glacial acetic acid. The reaction mixture was stirred for 3-4 hours at 40-45° until the tin dissolved completely. The tin was then precipitated electrolytically on a copper cathode and could be used in subsequent experiments. The catholyte was evaporated in vacuum. The residue was recrystallized from ethanol. The yield of hydrochloride was 0.35 g, i.e. 22% of theoretical. The dibenzoyl derivative had m. p. 178° (colorless crystals from ethanol). A mixed melting point with authentic dibenzoyl derivative of 1,4-diamino-2-butene [8] was not depressed.

2,3-Dichloro-1,4-dinitrobutane (IV). Into a three-necked flask of 150 ml capacity, fitted with a bubbler and a calcium chloride tube, were placed 11 g (0.075 mole) of 1,4-dinitro-2-butene, 75 ml of dry chloroform, and a few crystals of iodine. Over a period of 6-8 hours, 2 liters of dry chlorine was passed into the suspension, the reaction mass left overnight, and chlorination continued similarly for 3 more days. On the fifth day the colorless precipitate of the dichloride (IV) was collected and washed with a small amount of chloroform; the yield was about 8.5 g. The mother solution was chlorinated for a further 4-5 days to yield a further 4 g of dichloride. The total yield was 12.5 g (76% of theoretical) and the m. p. 115-117°.

1,3-Dichloro-1,4-dinitrobutane was a colorless crystalline product with m. p. 118° (from ethanol), which was readily soluble in acetone, dioxane, and glacial acetic acid and difficultly so in chloroform, ether, and ethanol.

$$\text{Found \% } \quad C \ 22.57, \ 22.62; \ H \ 3.07, \ 2.97; \ N \ 12.79, \ 12.89$$
$$C_4H_6Cl_2N_2O_4. \text{ Calculated \% } \quad C \ 22.12; \quad H \ 2.74; \quad N \ 12.91$$

1,4-Dinitro-1,3-butadiene (V). A mixture of 45 ml of glacial acetic acid, 4.34 g (0.02 mole) of dichloride (IV), and 8 g (0.02 mole) of lead acetate was gradually heated to 80° and kept at this temperature for 1 hour. After the reaction mixture had cooled, the precipitate of lead salts was removed by filtration and the acetic acid solution obtained was poured with stirring onto 200 ml of a mixture of ice and water; the precipitate of crude dinitrobutadiene was collected and dried. The yield was 1.2 g (40% of theoretical).

1,4-Dinitro-1,3-butadiene, which had m. p. 147-148° and formed yellow needles from chloroform or light-brown ones from ethanol, was readily soluble in acetone and glacial acetic acid and difficultly so in ether, chloroform, and ethanol.

Found %: C 32.91, 32.96; H 3.24, 3.28; N 19.76, 19.63
$C_4H_4N_2O_4$. Calculated %: C 33.36; H 2.80; N 19.44

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POLYMERIZATION AND COPOLYMERIZATION
OF DIENES AND OLEFINS ON A CHROMIC OXIDE CATALYST

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In the first communication it was shown that the polymerization of butadiene and isoprene on a chromic oxide catalyst yielded crystalline polymers, containing only 1,4-trans units in the chain [1].

In the present communication we describe polymers of 1,3-pentadiene and 1-butene and copolymers of dienes and olefins, obtained by polymerization on this catalyst.

The polymerization and copolymerization processes were under the same conditions as described in [1] at 80°, and in ligroin solution or in block. The monomer concentration in the solution was 3.3 mole/liter. The crystalline polymers were isolated by extraction from the swollen catalyzate with hot toluene. The copolymers were extracted from the catalyzate with solvent at room temperature. The polymers were precipitated from the solutions obtained with alcohol and dried in vacuum. Polymerization of 1,3-pentadiene, in contrast to butadiene and isoprene, gave an amorphous polymer with specific gravity 0.89, which was soluble in benzene. Its vitrification point was −60°. The unsaturation of the polymer was 97% of theoretical.

According to infrared spectroscopic data, the polymer did not contain side vinyl groups, indicating that fragments connected in the 3,4-position were absent from the chain. The bulk of the 1,4-units were attached in the trans-position.

TABLE 1

Properties of Polymers and Copolymers Based on trans-1,4-Dienes and Obtained by Polymerization on a Chromic Oxide Catalyst

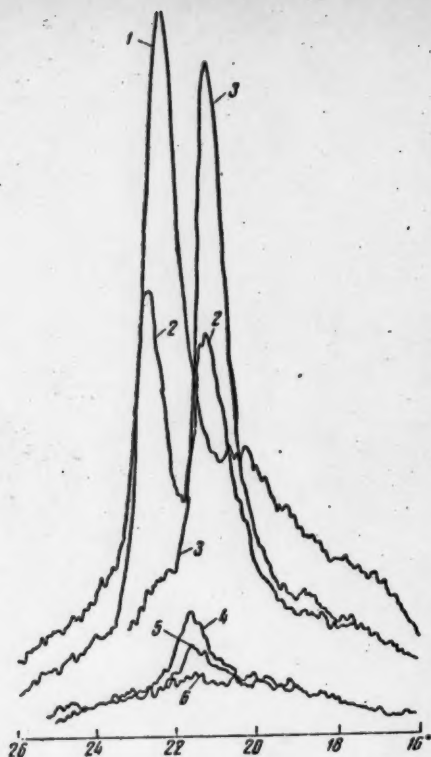| Monomers	Comp. of starting mixture I	Comp. of starting mixture II	Iodine number of polymer	Comp. of polymer, mole % I	Comp. of polymer, mole % II	Density of polymer	State	M. p. of crystals, °C	Vitrification point of polymer, °C
Butadiene			457			up to 1,015	Cryst.	135	(−110)
Isoprene			373			0,94			−71
1,3-Pentadiene			364			0,89—0,91	Amorph.		−60
1-Butene						0,96	Cryst.	145	
Butadiene (I) + isoprene (II)	50	50	425	59	41	0,918	Amorph.		−90
Butadiene (I) + 1,3-pentadiene (II)	50	50	419	53	47	0,910	"		−74
Isoprene (I) + ethylene (II)			322	72	28	0,908	"		−74
Butadiene (I) + propylene (II)			291	58	42	0,916			−76
	33	67	405	83	17	0,947	Cryst.		
	10	90	185	33	67	—	"		
Butadiene (I) + 1-butene (II)	20	80	380	83	17	0,95	"	130	

Fig. 1. X-ray scattering of poly-1-butene at various temperatures. 1) 20°; 2) 50°; 3) 60°; 4) 130°; 5) 140°; 6) 150°.

Polymerization of 1-butene on the chromic oxide catalyst yielded a crystalline, fibrous polymer, which was soluble in hot toluene and partially (about 30%) soluble in boiling diethyl ether. The specific gravity of the polymer was 0.96. Figure 1 gives curves of x-ray scattering for samples of poly-1-butene, plotted at different temperatures (from 20 to 150°).[*] The presence of the sharp maximum indicated the crystallinity of the polymer obtained. The melting point of the crystals, determined from the disappearance of the maximum, was about 140°. The data in Fig. 1 also indicate the presence of two crystalline modifications of poly-1-butene: modification I (angle $2V = 22.5°$) exists at temperatures up to 40° and modification II (with the angle $2V = 21.2°$) exists at temperatures of 60-140°. The two modifications exist over a narrow temperature range (about 50°).

On the example of natural rubber and guttapercha it was established that the vitrification points of polymers with cis- and trans-configurations of the units are practically identical (−71°). It might have been expected that the vitrification point of trans-polybutadiene was close to that of cis-polybutadiene (−110°). Disruption of the 1,4-trans structure by copolymerization of butadiene or isoprene with other compounds led to a loss in crystallization capacity by the polymer and its transition to a highly elastic state as is illustrated by the experimental data in Table 1.

The composition of the copolymer was calculated from data on unsaturation, determined by reaction with iodine chloride [3]. It should be noted that this method gives satisfactory results in determining the composition of a copolymer of a diene with a monoolefin. Its accuracy in determining the composition of a copolymer of two dienes such as butadiene and isoprene or butadiene and 1,3-pentadiene is considerably lower, as a change in the iodine number by one unit corresponds to a change in diene content of 1%. The copolymerization of mixtures of butadiene with isoprene and 1,3-pentadiene and also isoprene with ethylene yielded amorphous elastic products with vitrification points in the range between the vitrification points of the polymers from the corresponding monomers (see Table 1). Kinetic curves of polymerization of individual monomers and mixtures of them showed that in all cases mixtures of monomers polymerized more slowly than the separate monomers (Fig. 2). The copolymerization of an equimolecular mixture of butadiene and isoprene yielded an elastic, amorphous polymer with a vitrification point of −90°. Infrared spectroscopy[**] established that the butadiene and isoprene units in the chain were only in the 1,4-trans form. The specific gravity of the copolymer was 0.918 as compared with 0.94 for pure trans-polyisoprene and 0.98-1.015 for trans-polybutadiene, obtained on the same catalyst. From the unsaturation value (see Table 1), it was calculated that the polymer contained 55% of butadiene units. If there were a linear relation between the copolymer composition and its vitrification point, the latter for this sample should equal −92°. The structure of polybutadiene may be disrupted similarly by copolymerizing butadiene with 1,3-pentadiene. The vitrification point of the copolymer obtained by polymerizing a mixture of equimolecular amounts of butadiene and 1,3-pentadiene was −74°.

In the case of isoprene, the most interesting variant is coupling it with ethylene, as this leads to the formation of an amorphous trans-copolymer with a vitrification point below that of natural rubber. Isoprene was

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[*] The x-ray investigation of the polymers and copolymers was carried out by N. A. Andreeva on a URS-50 x-ray apparatus and with the radiation recorded by an ionization method according to the procedure described in [2].

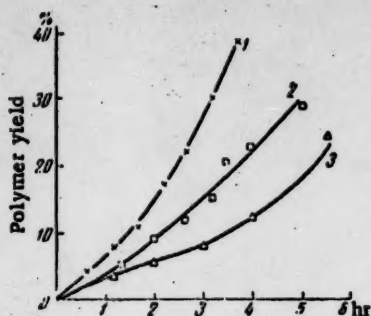[**] The infrared spectra were plotted by K. V. Nel'son.

Fig. 2. Kinetics of polymerization of butadiene (1) and isoprene (2) and co-polymerization of an equimolecular mixture of butadiene and isoprene (3) at 80° in ligroin solution.

copolymerized with ethylene at 90° in ligroin solution at an isoprene concentration of 1.8 mole/liter and an initial ethylene pressure of 30-36 atm. The polymers obtained were amorphous, had a comparatively low specific gravity (0.91-0.92), their ethylene content was 28 mole % (1st sample) and 42 mole % (2nd sample) and had vitrification points of −74 and −76°, respectively. If there were a linear relation between the vitrification point of copolymers and their composition, the vitrification point of pure polyethylene calculated from the data obtained is −84°.

In the case of butadiene, the transition to the highly elastic state could only be achieved by copolymerization with isoprene and 1,3-pentadiene. When propylene or 1-butene were introduced into the chain, even in comparatively large amounts, the polymers obtained were crystalline. It is known that a statistical distribution of about 15-20% of 1,2-units in a trans-polybutadiene chain converts the polymer to an amorphous, elastic state. Examples of this are butadiene polymers obtained by radical polymerization at low temperature [4, 5]. In the case we examined, the introduction of a considerable number of side ethyl and methyl groups into the chain did not change the polymer to an amorphous state. In this case we are apparently dealing with a mixture of crystalline polymers or with block-crystalline polymers.

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SYNTHESIS OF POLYVINYL ESTERS
OF PELENTANIC ACID

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One of us proposed a new method of using drugs in the treatment of various diseases which was directed at prolonging the action on the organism and (in certain cases) changing the qualitative character of the action [1]. The essence of this method consisted of chemical addition of the drugs (mainly organic) to polymeric, macromolecular chains of blood substitutes and introducing the drugs modified in this way into the blood. The blood substitutes proposed for this purpose in the first instance were various copolymers of vinylpyrrolidone (with vinyl alcohol, unsaturated acids, their amides and methylolamides, etc.), but other blood substitutes (for example, dextran) could also be used.

The presence of hydroxyl, carboxyl, amide, and methylolamide groups in these vinylpyrrolidone copolymers offers wide possibilities of adding to the copolymer chains drugs containing acid, alcohol, amide, amino, and imino groups by appropriate reactions in the chains of the macropolymers. These groups are contained in a wide variety of anti-tuberculosis, anesthetic, and antitumor preparations, in anticoagulants, etc. In some cases it is possible to prepare these modified drugs by copolymerization.

Thus, the method proposed is of very general importance. In solving the problem of modifying each separate drug it is sometimes necessary to develop an extremely complex chemical method of coupling it with the polymer (blood substitute), to establish the permissible number of drug molecules that can be added to the blood substitute macromolecule for the preparation to retain its plasma-substituting properties and to characterize the extent of the drug action of the preparation (bearing in mind the fact that the drug may substantially change its properties on incorporation into the polymer molecule of a blood substitute).

The purpose of the present investigation was to produce polymeric blood substitutes with anticoagulant properties. As the starting monomeric drug we chose the most effective coagulant among the 4-hydroxycoumarins. The first anticoagulant of this group was dicoumarin, which was isolated in 1940 from red clover [2] and found to have the structure of methylene-bis-(4-hydroxycoumarin) [3], which was reported by Anschutz as early as 1903. It was readily obtained by condensation of 4-hydroxycoumarin with formaldehyde in an aqueous medium.
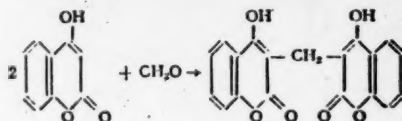
Until recently, dicoumarin was widely used as an anticoagulant (for treatment and prevention of infarcts, in thrombophlebitis, etc.). However, it has a high toxicity [4]. The best results are given by a 4-hydroxycoumarin derivative, so-called pelentan, which is the ethyl ester of di-(4-hydroxycoumarinyl-3)-acetic acid. Pelentan may be synthesized by the following scheme: a) preparation of (4-hydroxycoumarinyl-3)-acetic acid (pelentanic acid) by condensation of 4-hydroxycoumarin with glyoxylic acid:
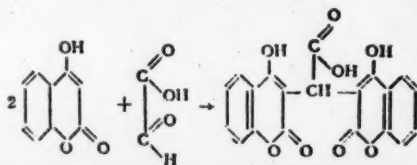
and b) subsequent esterification of pelentanic acid with ethyl alcohol. For esterification it is possible to use the acid itself (in the presence of H_2SO_4 or gaseous HCl) [5] or the lactone of pelentanic acid [6]. In the latter case the reaction proceeds very readily and gives a very pure preparation. To couple a 4-hydroxycoumarin derivative with a blood-substitute polymer we chose pelentanic acid (as the lactone), on the one hand, and a copolymer of vinyl alcohol and vinylpyrrolidone and pure polyvinyl alcohol on the other. The latter was used since work at the Leningrad Blood Transfusion Institute has shown that, contrary to certain reports [7], an aqueous solution of pure polyvinyl alcohol is a satisfactory plasma substitute. The pelentanic ester of polyvinyl alcohol was obtained by the reaction:
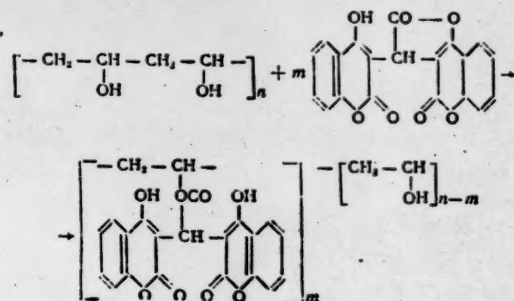
The reaction was carried out in pyridine at 97-98° for 2-3 hours. As a result of the reaction, the pelentanic esters of polyvinyl alcohol were obtained as the pyridine salt, which was readily decomposed with alkalis. Pelentanic esters of polyvinyl alcohol with a degree of substitution of 2-4 mole % (structurally these were copolymers of vinyl alcohol and the vinyl ester of pelentanic acid) were readily soluble in water, forming stable (not forming precipitates on long standing) solutions and retained the plasma-substituting properties of solutions of pure polyvinyl alcohol. This also applied to copolymers of vinylpyrrolidone with the vinyl ester of pelentanic acid, which were obtained by treating copolymers of vinylpyrrolidone and vinyl alcohol with the lactone of pelentanic acid. The latter copolymers were obtained by block copolymerization of a mixture of vinylpyrrolidone (95 mole) and vinyl acetate (5 mole) at 60-65° in the presence of azoisobutyrodinitrile with subsequent alcoholysis of the copolymer in absolute methanol in the presence of sodium methylate. After treatment with pelentanolactone in pyridine at 95-97° for 3 hours, the copolymers contained ~3 mole % of the vinyl ester of pelentanic acid.

The preparations obtained were tested in the Leningrad Blood Transfusion Institute (by M. A. Kotovschikova under the direction of Prof. L. G. Bogomolova) on rabbits and dogs. The experiments showed that the copolymer of vinyl alcohol and the vinyl ester of pelentanic acid, introduced intravenously as an aqueous solution, rapidly reduced the prothrombin content in the blood (when this solution with 25 mg of bound pelentanic acid was introduced into a rabbit, the prothrombin content was reduced to ~50% in a few hours and held at this level for a long period) and no visible side effects were detected.

Thus, on the example of anticoagulants (pelentanic acid) we confirmed the accuracy of the hypothesis [1] on the possibility of retaining the therapeutic action of drugs on their incorporation into the structure of a high-molecular blood substitute. A new qualitative effect in the use of pelentanic esters of polyvinyl alochol (apart from prolongation of the anticoagulant action) may be obtained (in connection with the speed of the reduction of prothrombin) where a rapid decrease in the coagulability of blood is required with high blood losses (during operations, etc.).

EXPERIMENTAL

4-Hydroxycoumarin. The technical product was recrystallized three times from 56% ethyl alcohol. The purified preparation had m. p. 113.5-114°.

Di-(4-hydroxycoumarinyl-3)-acetic acid (pelentanic acid). 4-Hydroxycoumarin (9.0 g) was dissolved in boiling 6% acetic acid (450 ml) and a hot 2% aqueous solution of glyoxylic acid added. Pelentanic acid precipitated after a few seconds and this was collected and dried. The yield was 80-82% of theoretical and the m.p. 215°. After recrystallization from acetone or 70% acetic acid, the product had m. p. 221.5-222°.

Lactone of pelentanic acid. Pelentanic acid (13.5 g) was dissolved in boiling 100% acetic acid (260 ml) and then a mixture of 100% acetic acid (10 ml) and acetic anhydride (4 ml) added. After an hour, the precipitated lactone was filtered from the hot solution. The yield was 75% of theoretical and the m. p. 270°.

Esterification of polyvinyl alcohol. Polyvinyl alcohol was obtained by alkaline alcoholysis of poly(vinyl acetate) with a viscosity of 20 centipoises. The dry powder of polyvinyl alcohol (1.2 g) was covered with pyridine (12 ml) and left to stand for 10-15 hours. Then 5-6 ml of pyridine was decanted and the same amount of fresh pyridine added with lactone (1.0 g). The flask was attached to a head with a stirrer, a mercury seal, and a reflux condenser protected from atmospheric moisture with a calcium chloride tube.

On stirring, the lactone rapidly dissolved in the pyridine in the cold to give a bright orange solution. When the lactone had dissolved, the flask was placed in a boiling water bath. After 5-7 minutes, the reaction mixture acquired a red-brown color and the polyvinyl alcohol swelled considerably. A thick, brown mass had formed after 20 minutes and then this hardly changed in external appearance. After 1 hour and 3 hours heating was stopped and the swollen product sucked free from reaction solution on a glass filter and washed with pyridine until the washing pyridine became clear.

The pyridine-swollen product (bright yellow color) was dissolved in water, precipitated with acetone and dried in vacuum at 35-40° and 10-15 mm Hg, and then in a vacuum desiccator over concentrated sulfuric acid. The reaction products obtained were the pyridine salt of the ester of pelentanic acid and polyvinyl alcohol with the following ester group content: after 1 hour esterification, 2.25 mole % and after 3 hours esterification, 2.50 mole % (21.6 weight %). (The ester group content was determined from the amount of NaOH bound and the excess alkali was titrated with 0.1 N HCl in the presence of methyl red.)

The dried esters formed coarse yellow flakes, which were readily ground to a powder. For removal of the pyridine, the esters were dissolved in water and the salt decomposed with sodium bicarbonate. The acid sodium salt of the pelentanic ester of polyvinyl alcohol was precipitated from the solution obtained with acetone, carefully washed with acetone and ether, and dried in vacuum at 35-40° and 10-15 mm Hg and then in a vacuum desiccator over concentrated sulfuric acid. A 2% aqueous solution of the sodium salt of the ester of pelentanic acid and polyvinyl alcohol (pH 7.6-7.9) was used for testing on animals.

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SOME POLYALKYLBENZENES

AND POLYALKYLCYCLOPENTYLBENZENES

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(Presented by Academician A. V. Topchiev, June 18, 1959)

In the present work we describe the synthesis of some polyalkylbenzenes (heptylxylenes) and polyalkylcyclopentylbenzenes; the position of the side chains in these hydrocarbons was determined from the ultraviolet absorption spectra. To prepare the heptylxylenes we alkylated the three isomeric xylenes with heptene under the action of concentrated sulfuric acid [1, 2].

The o-, m- and p-xylenes were purified by distillation on an efficient fractionating column of 40 theoretical plates and had properties close to literature values. The heptene was obtained by dehydrogenation of n-heptyl alcohol over aluminum oxide at 370° and had b. p. 95°/742 mm and n_D^{20} 1.4050, which correspond to heptene-1 with a certain amount of other isomers of this hydrocarbon. All the condensations were carried out with molar ratios of xylene : heptene : sulfuric acid of 3 : 1 : 1 with stirring and gradual addition of heptene and sulfuric acid to the xylene. The reaction mixture was periodically cooled with ice water. To convert the neutral sulfuric esters that were always formed in this reaction into acid esters the reaction product was treated 3-4 times with concentrated sulfuric acid and then the acid esters were extracted with alkali and water. The reaction products were distilled on a Fenske column of 12 theoretical plates and purified by chromatography on silica gel. The monoalkylate yield was 50-70% on heptene. Higher substitution products were not formed under these conditions.

TABLE 1

Properties of Polyalkylbenzenes and Polyalkylcyclopentylbenzenes

Hydrocarbon	B. p., °C/mm	Solid, p. °C	d_4^{20}	n_D^{20}	Aniline point (max.)
1,2-Dimethyl-4-heptyl-benzene	97—98°/3,5 251—252°/740	—65 (glass)	0,8721	1,4970	+2,5
1,3-Dimethyl-4-heptyl-benzene	91—92°/2 270°/760	—63 (glass)	0,8689	1,4950	+3
1,4-Dimethyl-2-heptyl-benzene	104°/6	—60 (glass)	0,8668	1,4941	—3
1,4-Dimethyl-2-heptyl-5-cyclopentylbenzene	164—166°/4 325—326°/760	—20 (glass)	0,9162	1,5157	+16
1,2-Dimethyl-4-tert-butyl-6-cyclopentylbenzene	127—128°,4	—28 (glass)	0,9234	1,5315	—8

In the condensation of o-xylene with a total amount of 72 g of heptene, the reaction products yielded a hydrocarbon with b. p. 97-98°/4 mm. Mol. weight found 203, 202; calc. 204.

Found % C 88,16; 88,23; H 11,89; 11,78
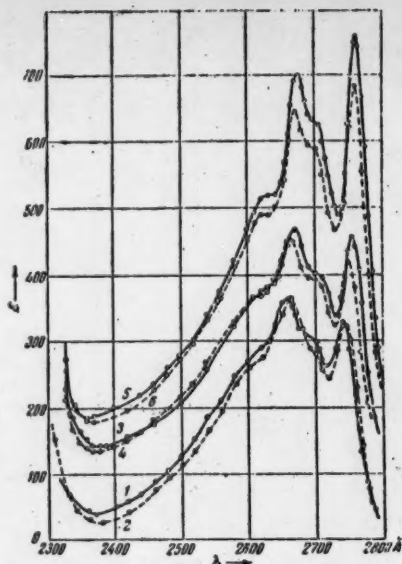
$C_{15}H_{24}$. Calculated % C 88,22; H 11,78

Fig. 1. Absorption spectra: 1) Heptyl-o-xylene, 2) isooctyl-o-xylene, 3) heptyl-m-xylene, 4) cyclohexyl-m-xylene, 5) heptyl-p-xylene, 6) cyclohexyl-p-xylene.
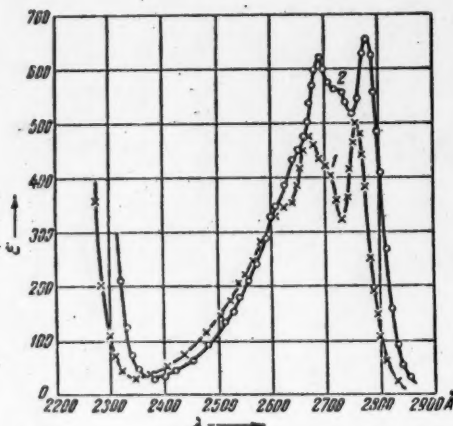

Fig. 2. Absorption spectra: 1) Pseudocumene, 2) durene.

The properties of the hydrocarbon and those of all the other hydrocarbons synthesized in the present work are given in Table 1.

Under analogous conditions, m-xylene and 43 g of heptene yielded the corresponding dimethylheptylbenzene.

Found %: C 88.05; 88.19;
H 11.72; 11.60

Reaction of 160 g of p-xylene with heptene under the conditions given above yielded 156 g of a hydrocarbon boiling at 104°/6 mm. Mol. weight: found 204, 205.

Found %: C 88.27; 88.18;
H 11.80; 11.82

The absorption spectra in the near ultraviolet region[*] were used to establish the position of the substituents in the hydrocarbons described. The absorption spectra of heptyl-o-xylene (A), heptyl-m-xylene (B) and heptyl-p-xylene (C), illustrated by curves 1, 3, and 5 in Fig. 1, have shapes characteristic of compounds of the pseudocumene type of structure (Fig. 2, 1). The differences observed between the spectra of the three isomeric heptylxylenes consisted of a gradual increase in intensity, an intensification of the first long-wave maximum, and a slight shift in the long-wave direction in going from compound A to B and C. This was caused by the different relative positions of the substituents in these compounds. As a general rule, the spectra of compounds with the same substituents in the para-position had these characteristics developed to a greater extent [5].

The pseudocumene character of the structure of compounds A, B, and C was confirmed by the great similarity of their absorption spectra to those of the following hydrocarbons (similar to them in the relative position of the substituents and in molecular weight): isooctyl-o-xylene (Fig. 1, 2) [5], cyclohexyl-m-xylene (Fig. 1, 4) and cyclohexyl-p-xylene (Fig. 1, 6) [3], respectively. The practically complete coincidence of the frequency characteristics of the spectra indicated that in all three cases the heptyl group was branched and attached to the benzene ring by a secondary carbon atom.[**] Thus, it can be considered established that the heptylxylenes synthesized were: 1,2-dimethyl-4-isoheptylbenzene, 1,3-dimethyl-4-isoheptylbenzene, and 1,4-dimethyl-2-isoheptylbenzene.

As was shown previously, the reaction of trisubstituted benzene with side chains in positions 1, 2, and 4 with cyclopentene under the action of aluminum chloride gave as the main product, benzene substituted in positions 1, 2, 4, and 5 and isomerization was not observed. We checked this hypothesis on the example of heptyl-p-xylene and cyclopentene.

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[*] The apparatus and procedure for the measurements were described previously [3-6].

[**] In the case of isooctyl-o-xylene, the benzene ring was also attached to a secondary carbon atom of the substituent [5].

TABLE 2

Position and Intensity of Characteristic Points of the Near Ultraviolet Absorption Spectra of the Hydrocarbons Synthesized (number before stroke — wavelength, after stroke — intensity)

| Hydrocarbon	Position λ, Å, and intensity ϵ of maxima, minima, and inflection points
1,2-Dimethyl-4-heptylbenzene	Max. 2740/326, min. 2718/260, inflec. 2690/308, max. 2655/362, inflec. 2600/268, min. 2370/42.0
1,3-Dimethyl-4-heptylbenzene	Max. 2755/355, min. 2730/236, inflec. 2705/300, max. 2670/367, inflec. 2620/274, min. 2380/43.0
1,4-Dimethyl-2-heptylbenzene	Max. 2763/616, min. 2735/344, inflec. 2705/480, max. 2675/552, inflec. 2620/368, min. 2360/38.0
1,4-Dimethyl-2-heptyl-5-cyclopentylbenzene	Max. 2788/646, min. 2752/543, max. 2700/638, inflec. 2610/368, min. 2425/114
1,2-Dimethyl-4-tert-butyl-6-cyclopentylbenzene	Inflec. 2765/181, inflec. 2730/216, max. 2670/270, inflec. 2580/191, min. 2410/50.0
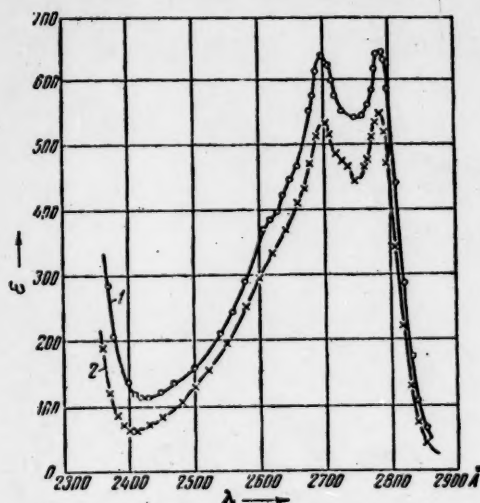
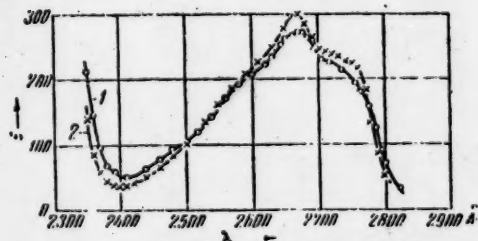Fig. 3. Absorption spectra: 1) Cyclopentylheptyl-p-xylene, 2) cyclopentylpsuedocumene.

Fig. 4. Absorption spectra: 1) Cyclopentyl-tert-butyl-o-xylene, 2) dicyclohexyl-o-xylene.

Two experiments on the condensation with a total of 89 g of heptyl-p-xylene and 22.5 g of cyclopentene (molar ratio 1 : 0.7) in the presence of aluminum chloride (18 g or 0.4 mole) yielded a hydrocarbon boiling at 164-166°/4 mm. Mol. weight: found 269, 274; calculated 272.

Found %: C 88.05; 87.95; H 11.98; 11.89
$C_{20}H_{32}$. Calculated %: C 88.17   H 11.83

The absorption spectrum of this compound (Fig. 3, 1) was similar in external form, with respect to both position and intensity, to the spectrum of durene (Fig. 2, 2) and that of cyclopentylpseudocumene, which has a durene-type structure (Fig. 3, 2) [3].

Consequently, the synthesis of the starting aromatic hydrocarbon proceeded without isomerization and the hydrocarbon obtained was 1,4-dimethyl-2-heptyl-5-cyclopentylbenzene.

A similar reaction was carried out with tert-butyl-o-xylene and cyclopentene in the presence of concentrated sulfuric acid. The given aromatic hydrocarbon was obtained by alkylation of o-xylene with isobutene in the presence of conc. H_2SO_4 by a previously tested procedure [8]. The hydrocarbon had b. p. 212°/747 mm; n_D^{20} 1.5000 and d_4^{20} 0.8721.

Reaction of 80 g of this hydrocarbon with equimolecular amounts of cyclopentene and conc. H_2SO_4 yielded a substance with b. p. 127-128°/4 mm. Mol. weight: found 222, 216; calculated 230.

Found %: C 88.48; 88.55; H 11.49; 11.50
$H_{17}C_{28}$. Calculated %: C 88.63;   H 11.37

Figure 4, 1 shows the absorption spectrum of the hydrocarbon obtained and this is characteristic of compounds with an isodurene-type structure and very similar in external form, with respect to both position and intensity, to the spectrum of the compound we synthesized previously, 1,2-dimethyl-3,5-dicyclohexylbenzene [3], which is similar to it in the relative positions of the substituents and molecular weight (Fig. 4, 2). Hence, it follows, the cyclopentyl group, which usually does not enter a position ortho to a methyl group, is completely unable to stand next to a tert-butyl radical and the compound synthesized was 1,2-dimethyl-4-tert-butyl-6-cyclopentylbenzene. 1,2-Dimethyl-4-tert-butyl-6-cyclopentylbenzene, 1,4-dimethyl-2-heptyl-5-cyclopentylbenzene and heptyl-m- and o-xylenes were prepared for the first time.

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